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## CONTENTS — INHOUD

*Page/Bladsy*

THE CHEMICAL CONCENTRATION AND SPECTROGRAPHIC DETERMINATION OF CERTAIN MINOR TRACE METALS IN PLANT MATERIAL *by* A. STRASHEIM AND D. J. EVE .. .. .. .. .. .. .. 1

ON THE PREPARATION OF POTASSIUM BROMIDE DISCS FOR INFRARED ANALYSIS *by* J. MORRIS AND S. J. VAN DER WALT .. .. .. 16

EFFICIENCY PARAMETERS IN LINEAR CHROMATOGRAPHY AND THEIR USE FOR ANALYTICAL PURPOSES *by* P. C. HAARHOFF AND VICTOR PRETORIUS .. .. .. .. .. .. .. .. 22

NOTES

RUTIN FROM *PACHYSTIGMA pygmaeum* *by* A. L. CLINGMAN .. .. 43

DISTRIBUTION COEFFICIENTS OF THE ANIONIC THIOCYANATE COMPLEXES OF METAL CATIONS *by* L. D. C. BOK AND V. C. O. SCHÜLER .. 66

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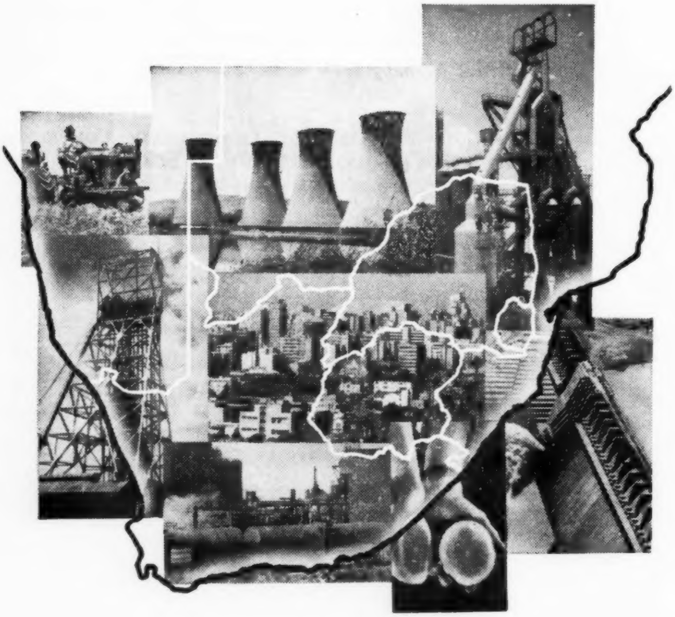

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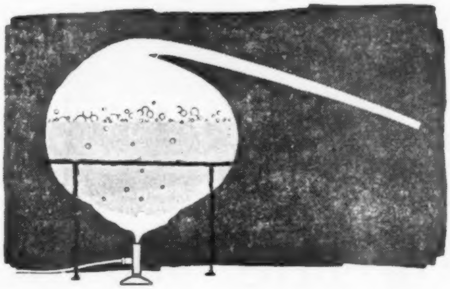

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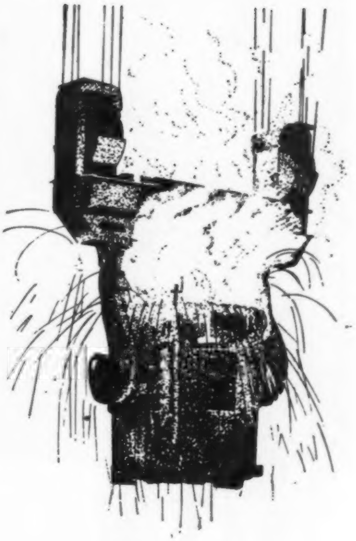

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Much of the results of chemical research in this country is published abroad. The following is a list of papers which have rècently appeared, and may be of use both to researchers here and overseas. It is intended to include such a list in each issue of this Journal and to make this list as comprehensive as possible.

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# THE CHEMICAL CONCENTRATION AND SPECTROGRAPHIC DETERMINATION OF CERTAIN MINOR TRACE METALS IN PLANT MATERIAL

*by*

**A. STRASHEIM and D. J. EVE***

## OPSOMMING

'n Metode word beskryf vir die spektrografiese ontleding van plantmateriaal vir sink, kobalt, nikkel, lood, titaan, vanadium, en molibdeen. Hierdie elemente word van yster en die ander bestanddele van die monsteroplossing geskei deur herhaaldelike chloroformekstraksie by voorafbepaalde pH-waardes, met gebruik van ditisoon, 8-hidroksie-kinolien en kupferron as kompleksreagense. Die gekombineerde ekstrakte, op grafietpoeier ingedamp, word in grafietmonsterelektrodes gepak en in 'n onderbreekte gelykstroomboog gebrand. Silver en kadmium word as interne standaarde gebruik. Van 'n plantmonster in oplossing gebring is sestien deelvolumes getrek en die herhaalbaarheid van die resultate bepaal. Die volgende variasiekoeffisiente is verkry:

Zn, 3·6%; Co, 14·5%; Ni, 6·4%; Pb, 22%; Ti, 11·6%; V, 11·3%; Mo, 10·6%.
Resultate van die ontleding van agt standaardmonsters word vergelyk met resultate deur ander metodes verkry. Die moontlikheid om koper en mangaam, as deel van die prosedure, deur vlamfotometrie te bepaal word aangetoon.

## SUMMARY

A method is described for the spectrographic determination of zinc, cobalt, nickel, lead titanium, vanadium, and molybdenum in plant material. These elements are separated from iron and from other constituents of a sample solution by successive chloroform extractions at predetermined pH values using dithizone, 8-hydroxyquinoline and cupferron as complexing reagents. The combined extracts are evaporated on to graphite powder, loaded into a graphite sample electrode and burned in an interrupted d.c. arc. Silver and cadmium were used as internal standard elements. The coefficients of variation calculated from analyses of sixteen aliquots of a solution of plant material are:

Zn, 3·6; Co, 14·5%; Ni, 6·4%; Pb, 22%; Ti, 11·6%; V, 11·3%; Mo, 10·6%.
Results of analysis of eight standard samples are compared with results obtained by other methods. The possibility of determining copper and manganese flame-photometrically as part of the procedure is demonstrated.

## INTRODUCTION

In most spectrographic methods developed for the determination of trace elements in plant materials, the trace elements are first separated from the major constituents of the sample. Both precipitation and solvent extraction methods have proved successful.

In the well established precipitation method developed by Mitchell and coworkers[1] and in some of the solvent extraction methods[2, 3, 4] the iron is concentrated with the other elements. It has been shown that unless the concentration of iron is kept constant[1, 3], or allowance made for variation in its concentration[4], the results can be seriously affected even when instruments of relatively high dispersion are used. With a low, or medium dispersion spectrograph, the presence of iron makes the quantitative determination of the minor trace metals exceedingly difficult. A concentration method in which the iron is separated from the elements to be determined, is therefore very desirable. Such procedures have been proposed by Gorbach and Pohl[5], by Doll and Specker[6] and by Wark[7]. In the latter, cobalt, zinc and copper are determined after their separation from iron and other sample constituents by extraction with dithizone in chloroform.

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Van Rooyen[8] has confirmed that the method proposed by Gorbach and Pohl can be applied to the analysis of plant material, but its many separations, involving repeated transfer of the sample solution from one vessel to another, make it both tedious and unsuitable for routine analysis. The procedure of Doll and Specker appears more promising. It has the practical disadvantages, however, that the sample solution must be prepared in 7N lithium chloride and the initial extraction made with a solvent less dense than water. In addition, some of the separations are unlikely to be completely quantitative. As yet no report has appeared of the successful application of this method to the quantitative analysis of plant material.

In this paper a concentration procedure is described which allows of the simultaneous spectrographic determination of zinc, cobalt, nickel, lead, titanium, vanadium and molybdenum after their concentration and separation from iron. Flame-photometric determination of copper and manganese in separate extracts is proposed as a possible adjunct to the analysis scheme.

## DEVELOPMENT OF THE METHOD

### 1. *Chemical separation and concentration of the trace elements.*

It is desirable that the sample solution should, as far as possible, remain in one vessel during the concentration procedure and in order that successive extracts may be simply tapped off from the separatory funnel in which the sample solution is retained, an extracting solvent denser than water is most convenient. Chloroform was found to be a suitable solvent and during the development of the method, with the needs of a routine laboratory in mind, attention was given only to readily available organic reagents which form metal complexes soluble in chloroform.

*Dithizone.* Since almost all of the iron in the sample solution could be expected to be in the form of ferric ions, which are not extracted by dithizone, dithizone extraction of zinc, cobalt, nickel and lead was a logical first step in the procedure. Extraction of these metals is normally carried out at alkaline pH with citrate or tartrate present to prevent the precipitation of hydroxides of iron and aluminium. Tests with sample solutions indicated that citrate was more efficient than tartrate in retarding the precipitation. A procedure involving the addition of ammonium citrate and similar to that described by Wark was therefore followed.

The influence of pH on the extraction of the metals concerned from 8% ammonium citrate solution was investigated for zinc, cobalt, nickel and lead and later for copper, cadmium and silver, the last two elements having been selected as internal standards. pH-extraction curves were plotted for each of the elements and these are shown in Fig. 1. Each point represents the percentage of the metal transferred to the organic phase after shaking for two minutes with 20 ml of 0·02% dithizone in chloroform, the metal concentrations being determined either colorimetrically or flame-photometrically. On the basis of these curves a pH of 9·5-10 was selected for the extraction. It was later observed that with some of the samples a light precipitate began to separate from solution at this pH but this did not interfere with the extraction.

*Oxine* (*8-hydroxyquinoline*). Investigation of the extraction of iron, titanium, vanadium and molybdenum with a 1% solution of oxine in chloroform indicated that, while a quantitative separation was not possible from tartrate solutions, the extraction of molybdenum and vanadium was sufficiently inhibited in the presence of 8% ammonium citrate to allow of the separation of iron from the latter elements at pH 3.

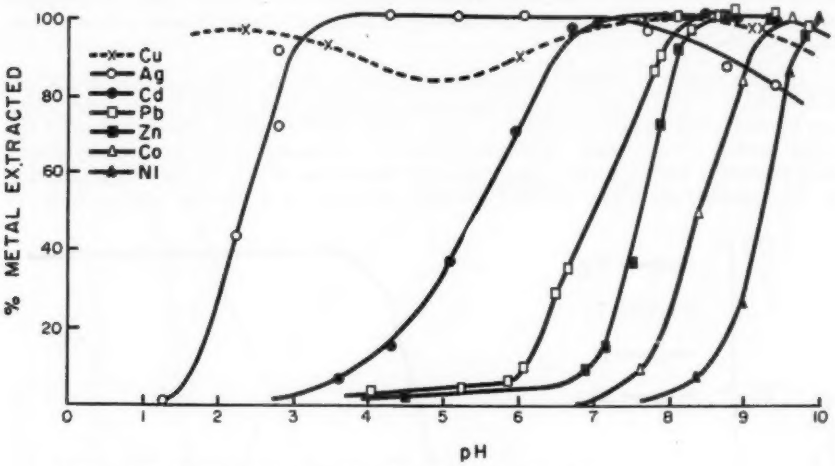


FIG. 1—Dithizone extraction of Cu, Ag, Cd, Pb, Zn, Co, Ni
Each point represents the percentage metal transferred to the organic phase after shaking for two minutes with 20 ml of 0.02% dithizone in chloroform. The metal concentrations Cu, Ag, Cd, and Pb were determined flame-photometrically while the concentrations of Zn, Co, and Ni were determined spectro-photometrically

In Fig. 2 the percentages of iron, titanium, vanadium and molybdenum removed from 8% citrate solution at various pH values by two extractions with 10 ml of 1% oxine are shown. The metal concentrations were determined colorimetrically in the case of iron and spectrographically in the case of titanium, vanadium and molybdenum.

Separation by oxine extraction at pH 3 is somewhat complicated by the fact that, at this pH, oxine is appreciably soluble in water[9] and repeated extraction leads to a building up of oxine concentration in the aqueous phase and consequent variation in conditions from one extraction to the next. In practice three or four extractions are necessary before most of the iron is removed. Extraction of a plant sample solution showed that the separation of iron from molybdenum and titanium was virtually complete and that at least 90% of the vanadium was unextracted.

*Cupferron.* Cupferron (ammonium N-nitrosophenylhydroxylamine) was selected for the extraction of titanium, vanadium and molybdenum, the method of extraction being based on that of Piper and Beckwith[10]. They found that molybdenum was extracted quantitatively from a 1·3% ammonium citrate solution at pH values below 1·0. Meunier[11] has reported that titanium, vanadium and molybdenum are precipitated by cupferron from solutions more acid than pH 1·8, but no detailed study of the cupferron complexes of these metals has been reported.

The influence of pH on the extraction of titanium, vanadium and molybdenum from 8% citrate solution was investigated and the results are shown in Fig. 3.

Solutions containing 50 micrograms of each metal were extracted once with 10 ml of pure chloroform after the addition of 1 ml of a freshly prepared 6% aqueous solution of cupferron and the extract analysed spectrographically. On the basis of these results titanium, vanadium and molybdenum were removed form the sample solution by a double extraction at about pH 2 and a further double extraction at about pH 0·5.

*Determination of copper and manganese.* Copper can be extracted with dithizone, either at pH 9·5 with the other dithizonates, or separately at pH 3, and manganese can be extracted from the sample solution with oxine at pH 8 after removal of the other metals. Both these elements, however, normally occur in concentrations inconveniently high for their spectrographic determination with the other elements in the concentrate. This difficulty may be overcome if a suitable aliquot only, of

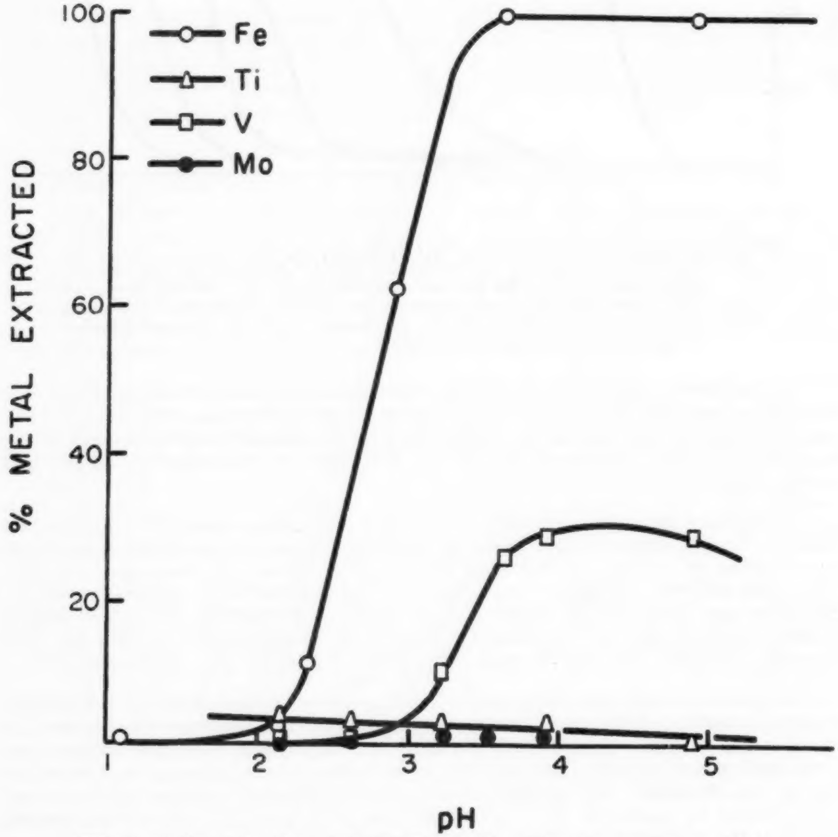


FIG. 2—Oxine extraction of Fe, Ti, V, and Mo, using two extractions with 10 ml of 1% oxine. The metal concentrations were determined colorimetrically in the case of Fe and spectrographically in the case of Ti, V, and Mo

the separate metal extract is added to the main concentrate, but it was found to be preferable to determine the concentrations of copper and manganese flame-photometrically. This can be done directly on the chloroform extract as has been proposed by Dean and Lady[12] or after evaporation and destruction of the extract with nitric and perchloric acid. Flame-photometric determination directly on the chloroform extract has the advantage of greater sensitivity, but, with the instrument used, the flame was inclined to behave erratically due to clogging of the burner jet. For this reason the figures given in this paper for copper and manganese were obtained from aqueous solutions after destruction of the organic extract.

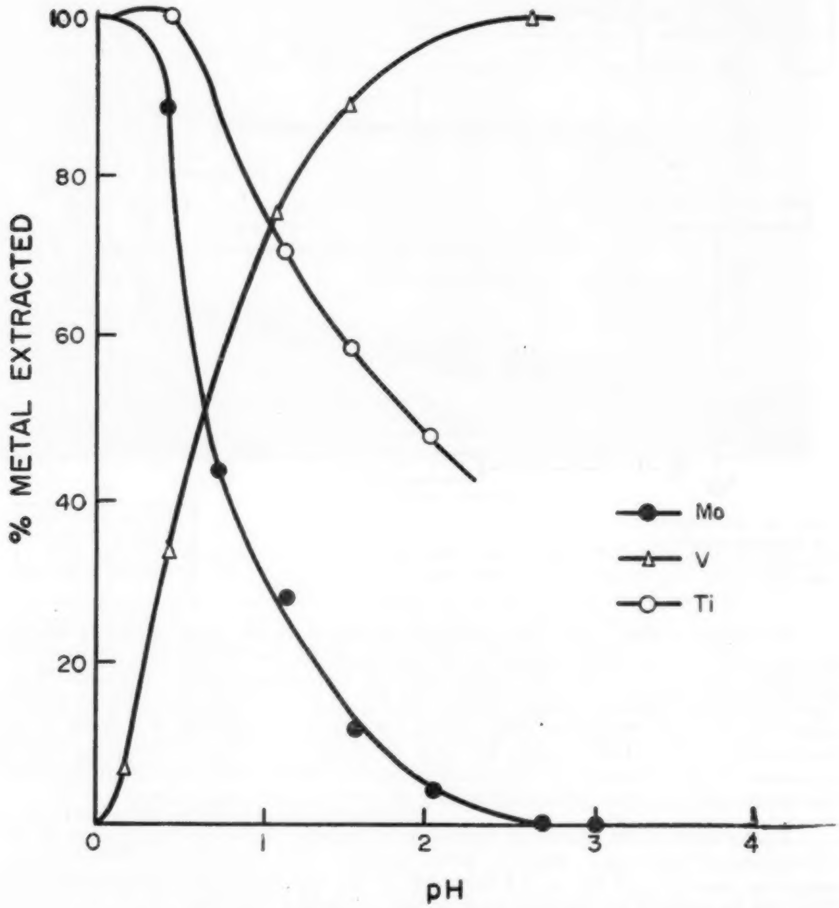
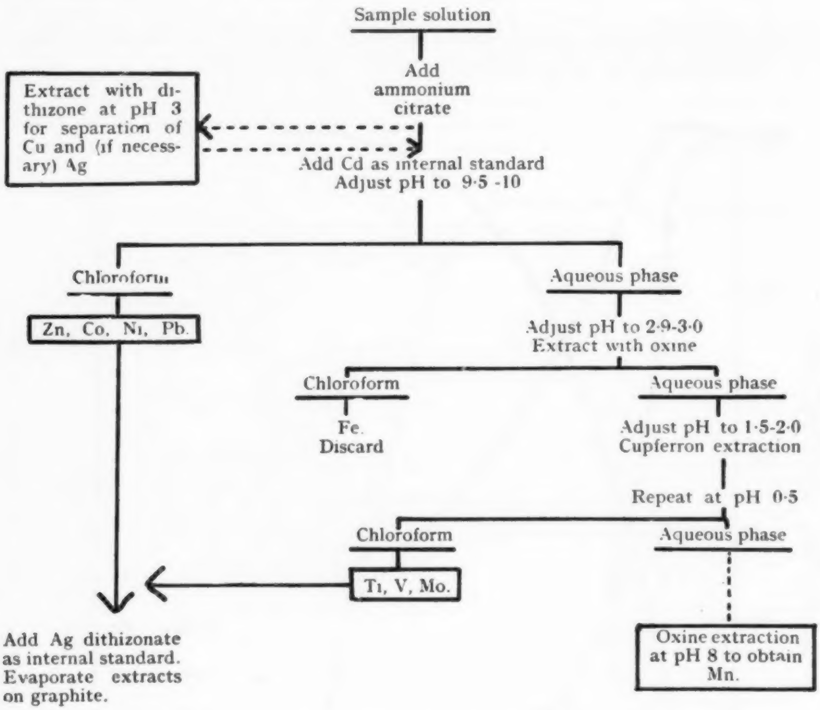


FIG. 3—Cupferron extraction of Ti, V, Mo, from 8% citrate solution. A single extraction with 10 ml of chloroform was used and elements were determined spectrographically

*The concentration procedure.* The concentration procedure adopted is shown in Table I.

TABLE I

*Flow-sheet of the concentration procedure*


Sample solution
Add ammonium citrate
Extract with dithizone at pH 3 for separation of Cu and (if necessary) Ag
Add Cd as internal standard
Adjust pH to 9·5 -10
Chloroform
Zn, Co, Ni, Pb.
Aqueous phase
Adjust pH to 2·9-3·0
Extract with oxine
Chloroform
Fe.
Discard
Aqueous phase
Adjust pH to 1·5-2·0
Cupferron extraction
Repeat at pH 0·5
Chloroform
Ti, V, Mo.
Aqueous phase
Oxine extraction at pH 8 to obtain Mn.
Add Ag dithizonate as internal standard. Evaporate extracts on graphite.

*Extraction method.* The concentration method demands fairly accurate adjustments of pH and an open separatory funnel, which allowed easy access of pH meter electrodes, was found more convenient than the conventional type. Agitation of the funnel's contents with an electric stirrer was found to produce perfectly satisfactory extraction and an apparatus (Fig. 4) was constructed consisting of a bank of six electrically driven glass stirrers, for each of which there was a clamp to hold a separatory funnel. With this apparatus six samples could be dealt with simultaneously, the whole concentration procedure taking about two and a half hours.

*Evaporation of the chloroform extract on to graphite.* Initially evaporation of the chloroform extracts on to graphite presented some difficulty as the solute tends to creep up the sides of the vessel from which the chloroform is being evaporated. This can be avoided by allowing some of the chloroform distilling off to reflux down the sides of the vessel. Wark[7] accomplished this by playing an air jet on the outside of the 1 ml beaker in which the final evaporation was carried out. The following method was found more satisfactory as it does not require constant attention.

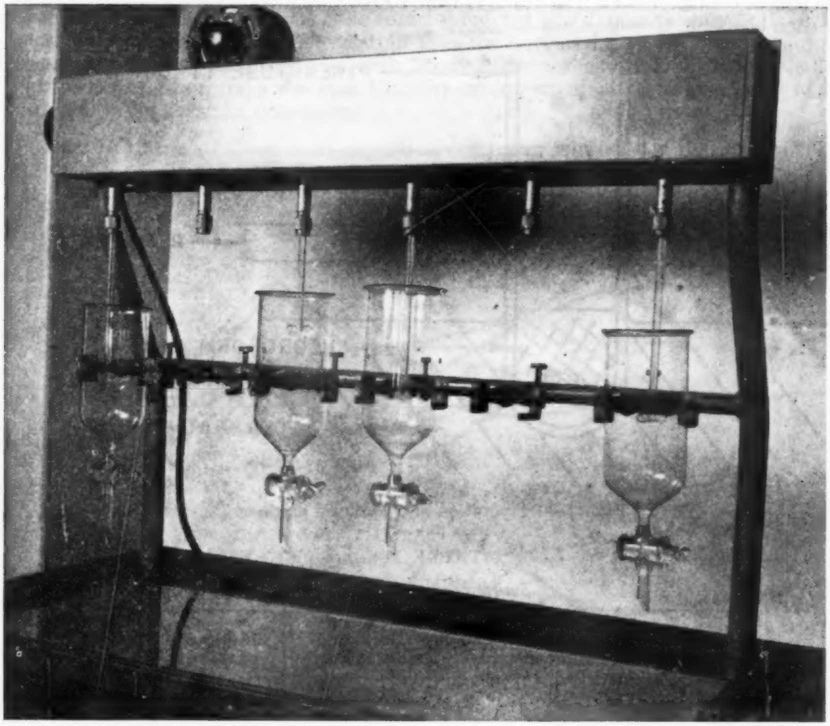


FIG. 4—Extraction apparatus

The apparatus used consisted of a glass tube mounted in a water bath as illustrated in Fig. 5. The chloroform extracts (first the dithizone extract and then the cupferron extract) were added a little at a time to the tube and the graphite (100 mg) added when there were only a few drops of chloroform left. During the last stages of the evaporation the tube was raised slightly from time to time to keep the liquid level inside it slightly above that of the water outside. If at any stage the extract appeared to be adhering to the walls of the tube all that was necessary was to remove it from the water bath and hold it in the air, or to blow on it gently. The graphite plus extract was dried first in the water bath, then in an oven at 100°C and finally for ten minutes in a muffle furnace at 450°C.

2. *Spectrographic analysis of the concentrate.*

*Excitation source conditions.* Most modern source units are built to provide interrupted arc conditions and a comparison of the performance and suitability for trace element determination of this type of excitation with the more commonly used d.c. arc seemed warranted. Experiments were therefore carried out with each. The d.c. arc was tested with and without an air jet of the type proposed by Stallwood[13] and current and buffer composition were varied with both types of excitation.

The source conditions listed in Table II were tested by plotting time intensity curves for each element.

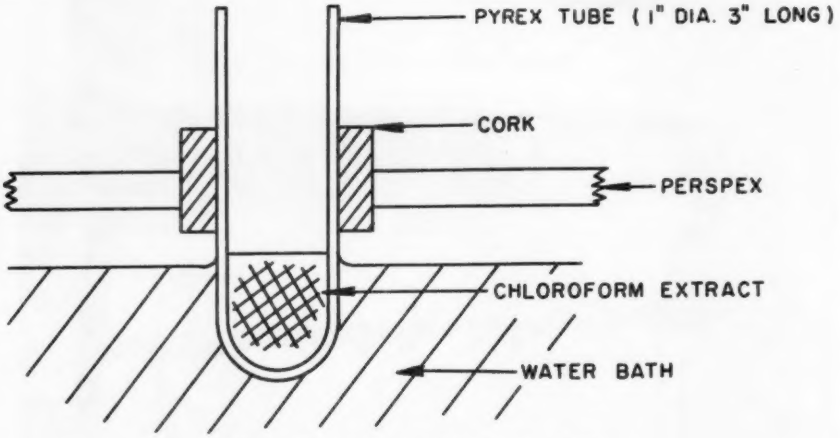


FIG. 5—Evaporation of chloroform extracts

TABLE II

*Source conditions tested*

| Source type | Condition | Sample electrode | Graphite buffer mixture | Current, amps | Electrode gap, mm |
|---|---|---|---|---|---|
| *Constant current d.c. arc* | (i) | 1 | 25% $Li_2Co_3$ | 10 | 9 |
| | (ii) | 1 | 42% $Li_2CO_3$ | 10 | 9 |
| | (iii) | 1 | 25% $Li_2CO_3$ | 5 | 9 |
| *D.c. arc with Stallwood air jet* | (iv) | 1 | 25% $Li_2CO_3$ | 10 | 9 |
| | (v) | 1 | 42% $Li_2CO_3$ | 5 | 9 |
| *Interrupted d.c. arc* | (vi) | 1 | 42% $Li_2CO_3$ | 3 | 4 |
| | (vii) | 1 | 42% $Li_2CO_3$ | 5 | 4 |
| | (viii) | 1 | 25% $Li_2CO_3$ | 4 | 4 |
| | (ix) | 2 | 42% $Li_2CO_3$ | 3 | 4 |

Sample electrodes. 1. Cavity depth 8 mm, internal diameter 2 mm, external diameter 4 mm.
2. Cavity depth 1 mm, internal diameter 4·5 mm, external diameter 6·4 mm.

The results showed that with a 10 amp d.c. arc the more volatile elements, lead and zinc were driven off in the early period of the arc with the less volatile elements showing strong emission only at the end. Increasing the concentration of lithium carbonate brought about only slight improvement. More even volatilisation was achieved using the air jet, but the interrupted arc was found to give both higher sensitivity and more even volatilisation than the normal d.c. arc. All but one of the tests were made with electrodes with 2 mm diameter cavities. A broad, shallow electrode (condition (ix) ) was found to give erratic results, due to wandering of the arc, and no increase in sensitivity.

On the basis of these tests condition (viii) was selected for the analysis. The results for conditions (v) and (viii) are shown in Figs. 6 and 7.

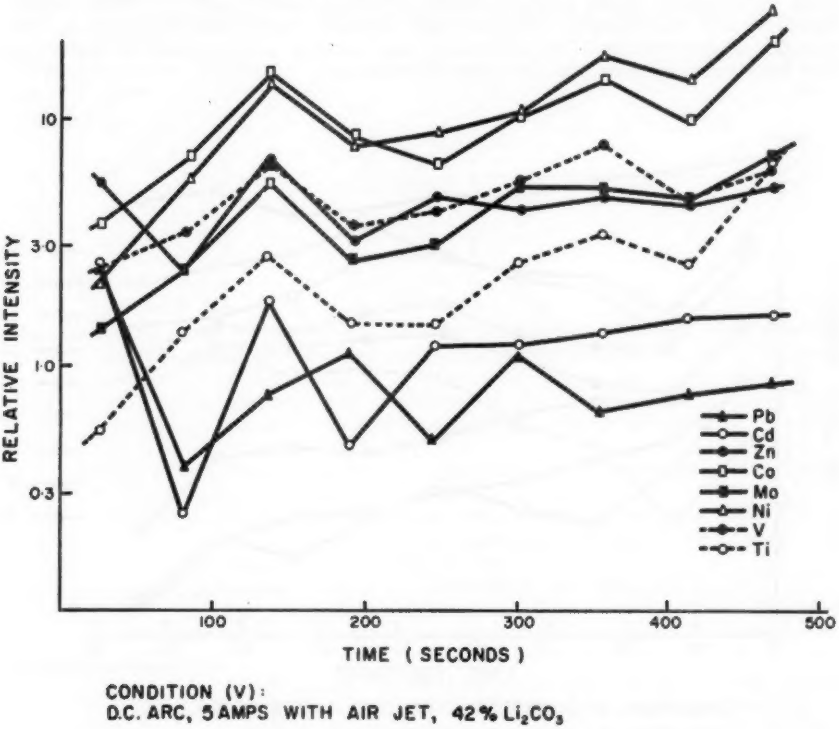


FIG. 6—Time-intensity curves
Condition (V): (Table II)
D.c. arc, 5 amps with air jet, 42% $Li_2CO_3$

*Internal standard elements.* After tests with a number of possible elements, cadmium was selected as internal standard for zinc and lead, and silver as internal standard for the other elements.

Both cadmium and silver form chloroform-soluble dithizonates, which means that they can be added to the extract solution before it is evaporated on to graphite, thus providing a control over this step. Cadmium has previously been shown to be a suitable internal standard for zinc[3, 14] and its time-intensity curve (Fig. 7) shows the same general trend as those of zinc and lead. Silver has been used as internal standard in the spectrochemical analysis of plants for cobalt, molybdenum and copper by Smit and Smit[15] who claim that the 3280·7Å line of silver is a perfect internal standard for these elements. When comparison is made with the elements for which it has been chosen as internal standard, silver is found to have an ionization potential of the same order and the excitation potential of the line used (3280·7Å) has a suitable value. The boiling point of silver (2212°C) is somewhat lower than those of the other elements (about 3000°C except Mo and Ti which are higher) but this is equally true of other possible internal standards. The time-intensity curve for silver consequently shows a slight downward trend, while those for cobalt, nickel, vanadium and molybdenum show a slight upward trend, and titanium a more pronounced upward trend. The differences are, however, less pronounced than could have been expected with other excitation conditions.

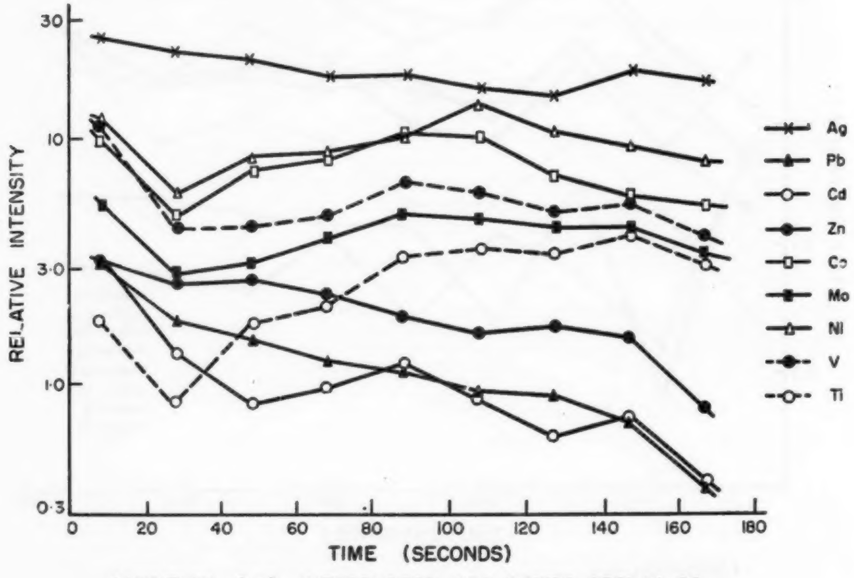


FIG. 7—Time-intensity curves
Condition (VII): (Table II)
Interrupted arc, 4 amps, 25% $Li_2CO_3$

The concentration of silver in plant material is normally too low (<0·05 p.p.m.) to interfere in the analysis, but, where higher concentrations of silver are expected, it can conveniently be removed with the copper in the sample by dithizone extraction at pH 3. No interference from silver present in the sample was observed in the samples analysed. The cadmium was added to the sample solution before extraction, but as there appeared to be some falling off in the efficiency of extraction of silver at high pH values, aliquots of a freshly prepared standard solution of silver dithizonate in chloroform were added to the dithizone extract before evaporation.

## EXPERIMENTAL

*Spectrograph.* Large Hilger Littrow with quartz optics. Wavelength range, 2550Å to 3850Å used.

*Source unit.* Interrupted d.c. arc source built in the laboratory.

*Microphotometer.* Double-projector microphotometer built in C.S.I.R. workshop.

*Photographic plates.* Ilford ordinary, developed in I.D.13 for 6½ minutes at 18°C.

*Emulsion calibration and calculation of intensity ratios.* A three-stepped neutral filter (100% : 33% : 9%) was used to give a stepped spectrum for emulsion calibration. Intensity ratios were calculated by the preliminary curve method (Churchill[16]) using an A.R.L. calculating board fitted with Seidel scales.

*Flame-photometer.* Beckman D.U. spectrophotometer with flame-photometric attachment.

*Analysis line pairs.*

| Element | Internal Standard |
|---|---|
| Zn 3345·0 Å | Cd 3261·1 Å |
| Co 3405·1 Å | Ag 3280·7 Å |
| Ni 3414·8 Å | Ag 3280·7 Å |
| Pb 2833·1 Å | Cd 3261·1 Å |
| Ti 3242·0 Å | Ag 3280·7 Å |
| V 3185·4 Å | Ag 3280·7 Å |
| Mo 3170·3 Å | Ag 3280·7 Å |

*Reagents.* All the reagents used were the purest available. Acids and ammonia were redistilled in glass. Distilled water was further purified by passage through an ion exchange column.

All aqueous solutions were stored in polythene bottles.

Dithizone. Prepared by dissolving Eastman Kodak dithizone in redistilled chloroform (0·02% w/v).

Oxine. Analytical grade 8-hydroxyquinoline dissolved in redistilled chloroform (1% w/v).

Cupferron. A 6% aqueous solution was prepared freshly for each set of analyses by mixing an appropriate quantity with water and filtering off the insoluble portion.

Ammonium citrate. The A.R. salt (400 g) was dissolved in water (1 L), ammonia added to pH 9 and the solution extracted with dithizone. Finally water was added and the solution made to 2 litres.

*Standard solutions.*

| | | |
|---|---|---|
| Zinc | 100 p.p.m. | Prepared by dissolving "Specpure" zinc oxide in a little dilute hydrochloric acid and diluting. |
| Cobalt | 200 p.p.m. | Prepared from analytical grade cobalt chloride. |
| Nickel | 1000 p.p.m. | Prepared from analytical grade nickel chloride. |
| Lead | 100 p.p.m. | Prepared from "Specpure" lead nitrate. |
| Titanium | 100 p.p.m. | Prepared from analytical grade potassium titanium oxalate. |
| Vanadium | 500 p.p.m. | Prepared by dissolving "Specpure" vanadium oxide in dilute sodium hydroxide, and the solution made slightly acid by addition of dilute hydrochloric acid. |
| Molybdenum | 100 p.p.m. | Prepared by dissolving $MoO_3$ in dilute sodium hydroxide and the solution made slightly acid with dilute hydrochloric acid. |

Portions of these solutions were mixed and suitably diluted just before running a series of standards to give a solution containing 10 p.p.m. Zn, 0·2 p.p.m. Co, 2 p.p.m. Ni, 1 p.p.m. Pb, 0·5 p.p.m. Mo, 10 p.p.m. Ti, 0·5 p.p.m. V. Suitable volumes of the latter solution were then treated in the same way as the sample solution.

*Internal standard solutions.*

| | | |
|---|---|---|
| Cadmium | 20 p.p.m. | Prepared by diluting a 500 p.p.m. solution prepared from "Specpure" cadmium sulphate. |
| Silver | 1 p.p.m. (in chloroform) | A 20 p.p.m. solution was prepared from "Specpure" silver nitrate. This solution (5 ml) was diluted slightly with sulphuric acid and extracted with dithizone. The extract was diluted to 100 ml with chloroform. |

*Standards for flame photometry.* These were prepared from analytical grade copper sulphate and manganese sulphate.

*Procedure.*

*Preparation of the sample solution.* A five gram sample of dried plant material was ashed in a muffle furnace at 450°C, the product extracted with hydrochloric acid (5N) and the residue dissolved in hydrochloric acid after fusion with sodium carbonate, as described by Mitchell[17].

*Dithizone extraction.* The solution was transferred to a 250 ml separatory funnel and 40 ml of 20% ammonium citrate and five ml of standard cadmium solution added. The pH was adjusted to about 9·5 by the addition of ammonia (1:1) and the solution agitated for two minutes with 20 ml of 0·02% dithizone. The extract was run into a beaker and the aqueous layer re-extracted, first with 5 ml of dithizone solution and finally with 5 ml of pure chloroform. If the final extract was pure green the extraction was regarded as complete, otherwise the extraction was repeated with 10 ml of the dithizone solution.

*Oxine extraction (removal of iron).* The pH of the solution was adjusted to 2·9-3·0 by the addition of hydrochloric acid and the solution extracted repeatedly with 20 ml portions of the oxine solution until the extract was only slightly coloured.

*Cupferron extraction.* The pH of the solution was further reduced to about 2 and after adding 2 ml of the cupferron solution it was extracted twice with 10 ml portions of pure chloroform. This extraction was repeated at pH 0·5.

*Preparation of the extracts for arcing.* A 5 ml aliquot of the standard silver dithizonate solution was added to the dithizone extract and the dithizone and cupferron extracts evaporated on to graphite by the method already described. After drying and ashing, the graphite-concentrate mixture was mixed with 33 mg of lithium carbonate and two sample electrodes were filled with portions of the final mixture (an "Elpac" electrode packing machine[18] was used).

*Spectrographic step.* The sample electrodes were burnt as anodes in an interrupted d.c. arc at 4 amps allowing a preburn of 30 seconds and an exposure of 2 minutes, duplicate spectra being recorded for each sample.

*Calculation of results.* The intensity ratios of analysis lines to internal standard lines were calculated and the concentrations read from standard calibration curves obtained by working through the above procedure with standard solutions.

The standard curves used to obtain the results reported here are shown in Fig. 8.

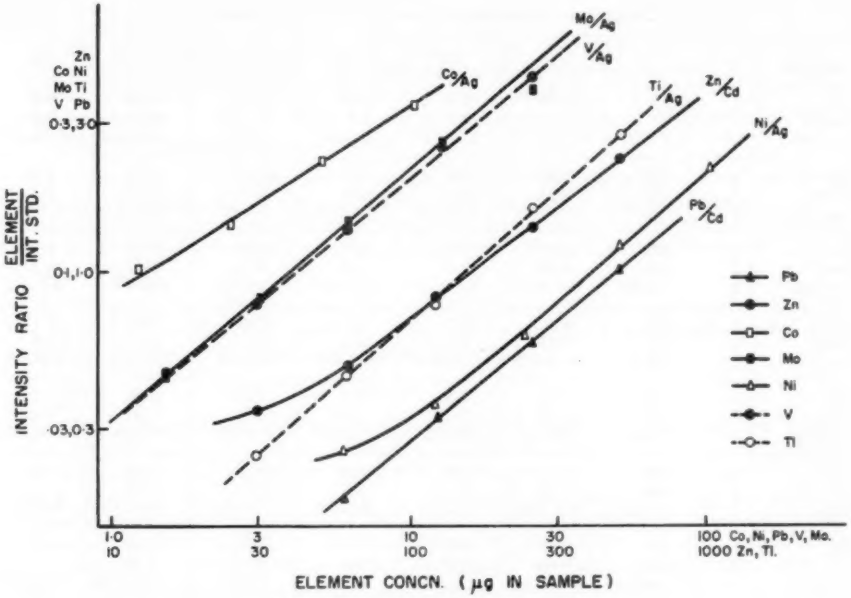


FIG. 8—Standard calibration curves

## RESULTS

To test the precision of the method, a solution of 100 grams of plant material was prepared and 16 aliquots of this solution, each equivalent to five grams of sample, were analysed. The results are shown in Table III.

TABLE III

*Results of analysis of sixteen aliquots of a solution of plant material*

| | Zn | Co | Ni | Pb | Ti | V | Mo |
|---|---|---|---|---|---|---|---|
| Mean results (p.p.m.) | 30·4 | 0·65 | 2·08 | 2·19 | 11·0 | 0·32 | 0·97 |
| Standard deviation (p.p.m.) | 1·10 | 0·094 | 0·133 | 0·49 | 0·128 | 0·036 | 0·103 |
| Coefficient of variation | 3·6% | 14·5% | 6·4% | 22·4%* | 11·6% | 11·3% | 10·6% |

*The last four aliquots seem to have become slightly contaminated.

The standard deviation for Pb on the first twelve analyses=0·3 p.p.m. or 16·4%.

In order to test the accuracy of the method, eight standard samples, which had been analysed previously by other methods, were reanalysed and the results compared. These results are shown in Table IV. Results of the flame-photometric determination of copper and manganese are similarly compared in Table V.

TABLE IV

*Comparison of analytical results (all values in p.p.m.)*

| Sample | | Zn | Co | Ni | Pb | Ti | V | Mo |
|---|---|---|---|---|---|---|---|---|
| 4A | 1* | 21 | 0·10 | 4·3 | 2·9 | 7·8 | 0·26 | < 0·2 |
| Peach | 2** | 24 | — | 2·7 | 2·6 | 11 | 0·24 | 0·06 |
| Leaves | 3*** | 21-28 | < 0·1-0·15 | 2·2-3·3 | 1·1-6·5 | 9-11 | 0·20-0·3 | 0·04-0·1 |
| 4B | 1 | 50 | 0·18 | 7·3 | 4·6 | 28·9 | 0·47 | 1·81 |
| Bean | 2 | 59 | 0·23 | 5·9 | 2·6 | 37 | 0·77 | 2·22 |
| Leaves | 3 | 56-60 | 0·1-0·36 | 4·8-6·6 | 1·5-3·9 | 32-42 | 0·51-1·0 | 1·7-3·5 |
| 4C | 1 | 25 | 0·27 | 2·8 | 2·3 | 19·2 | 0·40 | 0·74 |
| Beet | 2 | 23 | 0·23 | 2·5 | 2·2 | 21 | 0·52 | 1·27 |
| Leaves | 3 | 18-30 | 0·1-0·37 | 2·0-3·3 | 1·1-6·0 | 20-22 | 0·4-0·7 | 0·7-2·7 |
| 4D | 1 | 55 | 0·50 | 3·2 | 2·3 | 27·9 | 0·40 | 2·10 |
| Gem | 2 | 49 | 0·33 | 3·3 | 4·4 | 41 | 1·0 | 4·5 |
| Leaves | 3 | 38-60 | 0·15-0·5 | 3·0-4·0 | 2·7-5·5 | 40-42 | 0·9-1·1 | 3·3-5·5 |
| 4E | 1 | 49 | 0·46 | 1·4 | 3·5 | 6·8 | 0·29 | < 0·2 |
| Plum | 2 | 60 | 0·65 | 1·4 | 2·3 | 8·5 | 0·24 | — |
| Leaves | 3 | 30-93 | 0·49-0·8 | 0·19-2·1 | 0·5-5·5 | 7·7-9·3 | 0·13-0·3 | 0·05-1·5 |
| 4G | 1 | 30 | 0·73 | 2·2 | 1·9 | 11·6 | 0·39 | < 0·2 |
| | 2 | 30 | 0·41 | 4·4 | 1·2 | 27 | 0·70 | — |
| Bush | 3 | 25-41 | 0·3-0·63 | 2·5-6·5 | 0·5-1·7 | 23-31 | 0·68-0·72 | 0·03-8 |
| 4H | 1 | 34 | 0·84 | 8·7 | 1·7 | 18·3 | 0·57 | < 0·2 |
| | 2 | 37 | 0·93 | 7·9 | 0·8 | 17 | 0·36 | — |
| Tobacco | 3 | 28-50 | 0·8-1·2 | 2·1-12·5 | 0·2-2·0 | 16-18 | 0·25-0·46 | 0·04-0·2 |
| 4I | 1 | 50 | 1·95 | 15·2 | 0·9 | 80·8 | 2·18 | < 0·2 |
| | 2 | 51 | 2·19 | 13·5 | 1·2 | 74 | 2·51 | — |
| Tobacco | 3 | 45-76 | 1·74-2·9 | 11·6-17·0 | 0·5-2·0 | 65-83 | 1·5-4·0 | 0·05-0·5 |

*1 Results obtained by the method described.
**2 Average value of various other methods used to analyse samples (Strasheim and Camerer[14])
***3 Range of results of the other methods.

TABLE V

*Comparison of analytical results for copper and manganese (all values in p.p.m.)*

| Sample | Method | Cu | Mn |
|---|---|---|---|
| 4A | 1* | 7·9 | 45 |
| | 2** | 6·1 | 43·2 |
| | 3*** | 4-8·7 | 12-58 |
| 4B | 1 | 11·5 | 38 |
| | 2 | 12·0 | 37 |
| | 3 | 9·6-12·9 | 17-53 |
| 4C | 1 | 9·1 | 120 |
| | 2 | 11·8 | 146 |
| | 3 | 8·4-15 | 69-182 |
| 4D | 1 | 5·3 | 100 |
| | 2 | 6·1 | 121 |
| | 3 | 4·3-9 | 60-150 |

* Results obtained by the method described .
** Average value of various other methods used[14].
*** Range of results of the other methods.

The precision of the method as indicated by the coefficients of variation, is very good in the case of zinc, and quite adequate for nutritional studies in the case of other elements, with the possible exception of lead. It is evident from previously reported results[14], that analysis for the latter element presents peculiar difficulties, possibly due to reagent contamination.

Because of poor agreement between the previous analyses of the "standard" samples, it is difficult to draw definite conclusions as to the absolute accuracy of the method. In most cases the results show the same trends as the means of previous results. In general it can be concluded that the accuracy compares well with that of other methods.

The sensitivity of the method in the case of molybdenum is not as high as might be desired. This difficulty might be overcome by using a larger sample or by using half the amount of graphite and lithium carbonate.

## CONCLUSIONS

The concentration method described is both rapid and suitable for routine use. A fairly wide range of trace elements can be determined using the method, but the procedure could readily be simplified where only some of these elements are to be determined, and a study of the knowledge gained about the organic reagents, suggests a number of possible modifications for the determination of selected groups of elements. The advantage of the interrupted arc source for the simultaneous determination of a wide range of trace elements has been demonstrated, but the method could undoubtedly be used successfully in conjunction with d.c. arc excitation, when condition (v) (Table II) is recommended.

The authors are indebted to Miss E. C. Maskew for her assistance with some of the analyses and to the Department of Agriculture and the Macaulay Institute for Soil Science for their analyses of the plant samples used.

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# ON THE PREPARATION OF POTASSIUM BROMIDE DISCS FOR INFRARED ANALYSIS

*by*

**J. MORRIS and S. J. VAN DER WALT**

## OPSOMMING

Ondersoek is ingestel na die uitwerking van die omstandighede waaronder kaliumbromiedplaatjies voorberei word op hul optiese deurlaatbaarheid en stabiliteit. Streng voorsorgmaatreels teen die adsorpsie van water op die alkalihalied moet getref word om deursigtige plaatjies te verkry. Optimum omstandighede vir maksimum deurlaatbaarheid en stabiliteit behels dus die droging van die gemaalde en gesifte kaliumbromied vir ses uur by 400°C en 'n druk van 0·05 mm, toevoeging en vermenging van die monster in 'n droogkas, terwyl die poeier vir een minuut onder 'n druk van 7050 kg $cm^{-2}$ geplaas en die pers tot 2 mm ge-evakueer word.

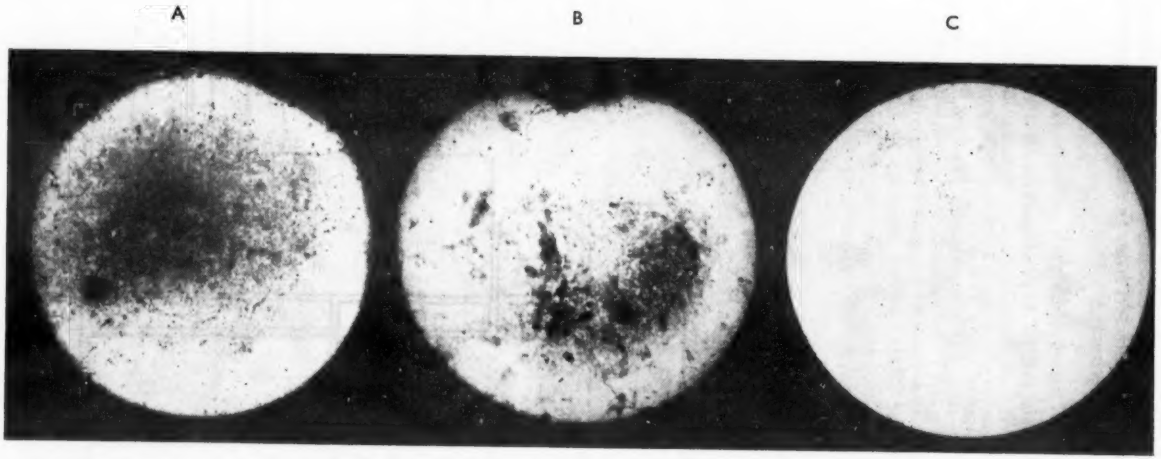
## SUMMARY

The influence of the conditions for the preparation of potassium bromide discs on their optical transparency and stability has been investigated. Strict precautions against the adsorption of water on the alkali halide have to be observed to ensure transparent discs. Optimum conditions for highest transmittance and stability therefore comprise drying the ground and sifted potassium bromide for six hours at 400°C under a pressure of 0·05 mm, adding and mixing the sample in a drybox and pressing for one minute at 7050 kg $cm^{-2}$ while evacuating to a pressure of 2 mm.

Discs prepared in our Laboratory from Mercks AR-grade potassium bromide often exhibited considerable unwanted absorption in the infrared region, ranging from almost total absorption at 5000 $cm^{-1}$ to a normal background at about 2000 $cm^{-1}$. With the rocksalt prism of low dispersive power in the region 5000-1700 $cm^{-1}$ it is relatively difficult to distinguish between OH, NH and CH absorption bands without the complication of an extremely high background and a strong absorption band at 3410 $cm^{-1}$ due to moisture adsorbed on the potassium bromide. The following investigation was undertaken with a view to determining why some discs should be more opaque than others and whether the expense of using commercially available specially prepared potassium bromide instead of the normal laboratory reagent would be justified.

Two different kinds of opacity were observed. Soon after the disc was taken from the die, a "fogging" of the surface took place which slowly increased with time. The transmittance, however, remained unaffected except for a slight increase in the intensity of the OH absorption peak.

The second type of opacity was of a more serious nature. Mat areas (Fig. 1b) frequently appeared in freshly prepared discs, from where the opacity would spread, ultimately covering the whole area of the disc (Fig. 1c). The growth of those areas could be followed optically and invariably resulted in total absorption (Fig. 4, lower line). It appeared that an internal change was responsible for the unwanted effect, as the surface of the discs remained unaltered. X-ray analysis of totally opaque discs showed only normal potassium bromide structure.



**A: "Vacuum-pressed" disc. B and C: Various stages of opacity in "non-vacuum" KBr pellets.**

FIG. 1—Varying opacity of potassium bromide pellets

Although the potassium bromide technique for infrared analysis is well established, examination of the literature revealed wide variations in the experimental conditions. Table I shows data collected from the literature regarding the different experimental variables of the technique.

TABLE I

*Experimental data for the potassium bromide technique*[1]

| Ref. | Applied pressure, kg/cm $^2$ | Period of compression, seconds | Vacuum, mm | Thickness, mm |
|---|---|---|---|---|
| 2 | 4,935 | — | — | 1 |
| 3 | 6,500 | 0·5 | — | — |
| 4 | 7,060 | 300 | 15 | 0·5-2·0 |
| 5 | 7,200 | 600 | — | — |
| 4 | 8,030 | 120 | — | — |
| 6 | 9,070 | — | — | — |
| 7 | 9,870 | 60 | ·04 | — |
| 8 | 10-11,000 | 60-120 | — | — |
| 9 | 22,550 | 300 | — | — |

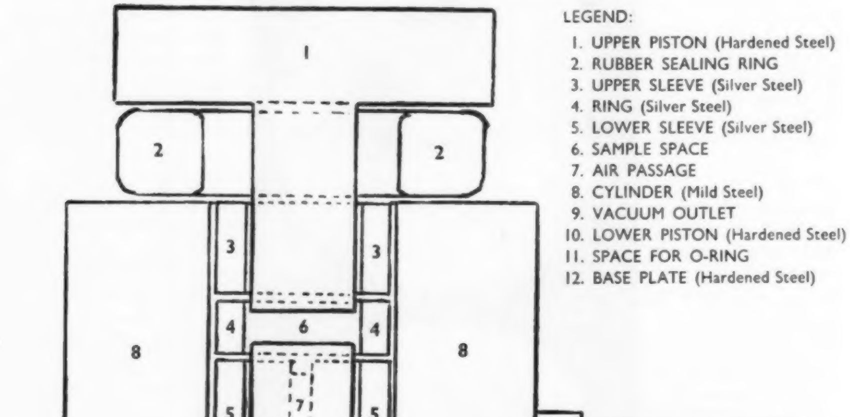

LEGEND:
1. UPPER PISTON (Hardened Steel)
2. RUBBER SEALING RING
3. UPPER SLEEVE (Silver Steel)
4. RING (Silver Steel)
5. LOWER SLEEVE (Silver Steel)
6. SAMPLE SPACE
7. AIR PASSAGE
8. CYLINDER (Mild Steel)
9. VACUUM OUTLET
10. LOWER PISTON (Hardened Steel)
11. SPACE FOR O-RING
12. BASE PLATE (Hardened Steel)
1
2
2
3
3
4
6
4
8
8
5
7
5
9
10
11
11
12

FIG. 2—Evacuable die for potassium bromide pellets

A die similar to those described by Olsen[6] and Pickering[10] was designed. This allowed easy evacuation of the sample space prior to, and during pressing, (Fig. 2); a sample holder was furthermore designed to fit onto the standard Perkin-Elmer cell holder.

Different sets of experiments were carried out in which the pressure, concentration, and the time during which the discs were subjected to pressure, were varied. Fig. 3 shows the variation of the transmittance at 5000 $cm^{-1}$ with applied pressure. Increasing the pressure above 7000 kg $cm^{-2}$ therefore does not serve any useful purpose. Using a 12·5 mm circular disc and 250 milligrams of potassium bromide, the concentration of the sample in the matrix (0·3-0·7%) was not critical, provided the absolute amount of sample remained in the range of 0·9 to 1·2 milligrams. Prolonging the application of pressure beyond sixty seconds did not result in any improvement of the transmittance. After compressing the powder for less than a minute or at pressures lower than 5700 kg $cm^{-2}$, traces of uncoalesced potassium bromide could be seen.

Three different samples of potassium bromide were prepared by drying the salt for (a) four hours in air at 100°C, (b) six hours in air at 500°C, (c) six hours at less than 0·05 mm pressure at 400°C.

Blank discs were prepared by grinding 250 milligrams of the dried potassium bromide (fineness —325 mesh) in a Wig-L-Bug machine for one minute and then

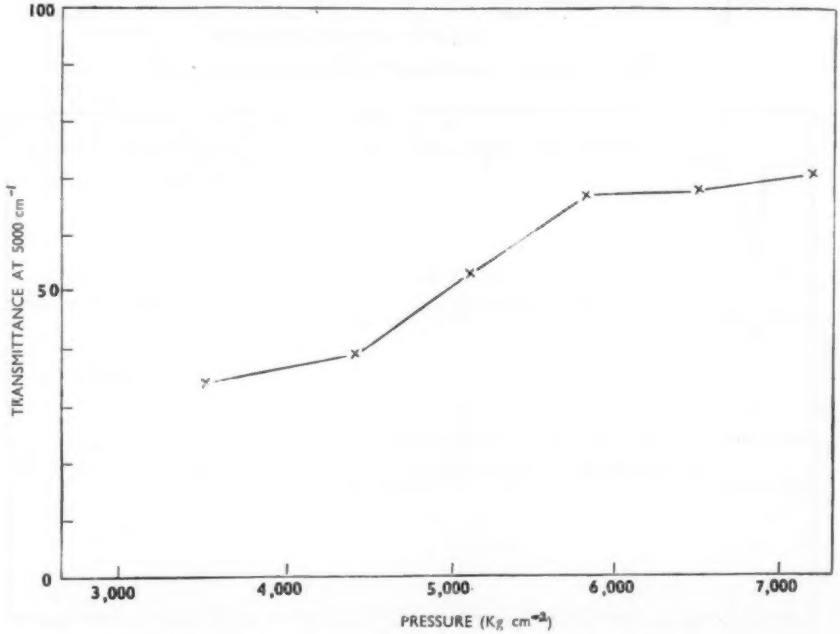


FIG. 3—Pressure-transmittance relation of potassium bromide pellets

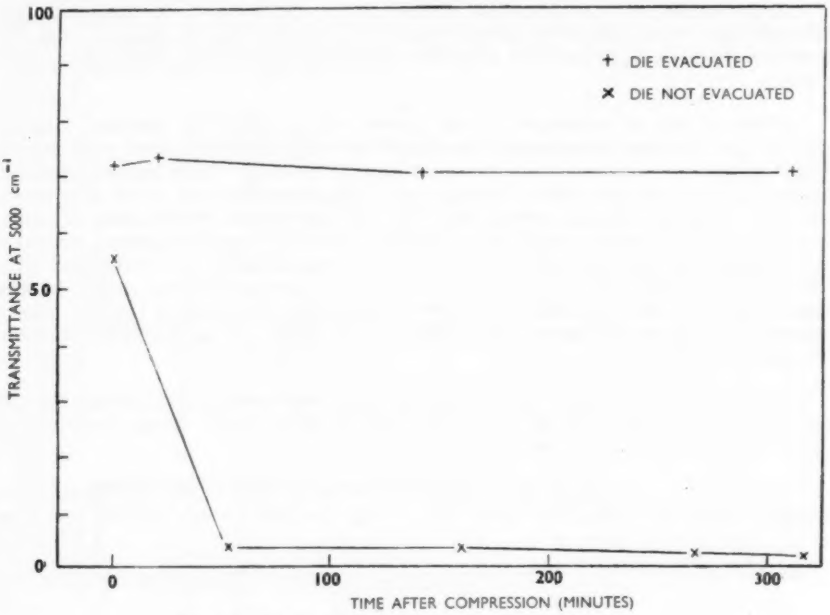


FIG. 4—Infrared spectra of potassium bromide discs

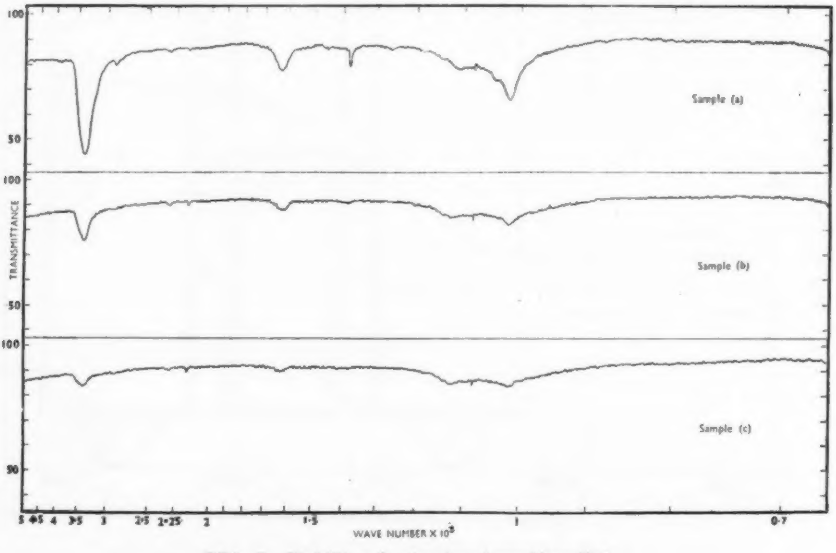


FIG. 5—Stability of potassium bromide pellets

transferring the powder to the die. These operations were carried out in a drybox.* The sample was then subjected to a pressure of 7050 kg $cm^{-2}$ for one minute. Spectra were run on a Perkin-Elmer Model 21 spectrophotometer.

The results of these tests are shown in Fig. 5. It is evident that a worthwhile reduction in the intensity of absorption by the adsorbed hydroxyl groups is obtained by drying the halide under vacuum. It was found that exposure of the powder for as little as a few seconds to the laboratory atmosphere (relative humidity ca. 30%) resulted in an increase of the OH absorption.[11]

A very notable improvement in the stability of the transmittance and the overall quality of the discs was obtained by evacuating the die to about 2 mm just before and during the period of pressing (Fig. 4).

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*The drybox consisted of a rectangular compartment (30x40x50 cm) made of Perspex through which a rapid stream of air (filtered and dried by passing through (a) cottonwool. (b) concentrated sulphuric acid, and (c) twice through silica gel) was passed. Manipulation of equipment was effected by means of rubber gloves set into the walls of the box.

# EFFICIENCY PARAMETERS IN LINEAR CHROMATOGRAPHY AND THEIR USE FOR ANALYTICAL PURPOSES

*by*

**P. C. HAARHOFF and VICTOR PRETORIUS**

## OPSOMMING

Metodes waardeur die totale- en kolomeffektiwiteite van lineêre chromatografiese prosesse gemeet kan word is bestudeer. Verskillende sulke mate, wat algemeen van toepassing is en wat maklik uit die chromatogram van die mengsel bepaal kan word, is ontwikkel. Die gebruik van effektiwiteitsparameters in analitiese chromatografie is bespreek, met besondere verwysing na die waardes van hierdie parameters wat benodig word om 'n gegewe skeiding tussen twee stowwe te bewerkstellig.

## SUMMARY

A study has been made of methods of measuring the overall and column efficiencies of linear chromatographic processes. Several such measures, which are of general applicability and which may be readily determined from the chromatogram of the solutes, have been developed. The use of efficiency parameters in analytical chromatography has been discussed, with particular reference to the values of these parameters which are required to separate two solutes to a given extent.

### *Efficiency parameters in linear chromatography*

The *overall efficiency* with which a given pair of solutes are separated by means of linear chromatography depends on two factors[1]: the *solvent efficiency* and the *column efficiency*. The solvent efficiency is characterized by the *separation factor*[2], $\alpha$, where*

$$\alpha=\frac{k_2}{k_1} \qquad \ldots \quad (1)$$

In gas-liquid chromatography, $\alpha$ is also known as the *relative volatility*. Since[3]

$$k=\frac{\bar{v}-v_g}{v_g} \qquad \ldots \quad (2)$$

it follows that

$$\alpha=\frac{\bar{v}_2-v_g}{\bar{v}_1-v_g} \qquad \ldots \quad (3)$$

$\alpha$ may thus be determined from the approximate equation[1, 4]

$$\alpha=\frac{\bar{v}_2}{\bar{v}_1} \qquad \ldots \quad (4)$$

provided that the solutes are strongly retarded, i.e. that $k_2$, $k_1 \gg 1$ and $\bar{v}_2$, $\bar{v}_1 \gg v_g$. When $k_2$ and $k_1$ are small, which is frequently[5] the case in the columns used at present, the apparent[6] or nett retention volumes $(\bar{v}_2 - v_g)$ and $(\bar{v}_1 - v_g)$, and not the (total) retention volumes $\bar{v}_2$ and $\bar{v}_1$, should, however, be used to estimate the solvent efficiency, as may be seen from equation (3). The column efficiency is determined by the broadening of the solute bands as they pass through the column, and has previously been measured, for each solute, in terms of the number, N, of theoretical plates,[7] where

---

*The symbols are defined at the end of the paper.

$$N = \left(\frac{\bar{v}}{\sigma}\right)^2 = 16\left(\frac{\bar{v}}{w}\right)^2 \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \quad (5)$$

$N_1$ and $N_2$ will generally differ, and an average value is then employed[4]. When a solute is strongly retarded, N is an adequate measure of the column efficiency. Purnell has recently shown[8] that when k is small, this is no longer true, and also that serious errors[5] may result from the use of N. The same author has proposed that the column efficiency be described in terms of a parameter

$$S = 16\left(\frac{\bar{v} - v_g}{w}\right)^2 \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \quad (6)$$

The arguments leading up to this proposal have been concerned with a somewhat simplified chromatographic model. In the present study efficiency parameters which are applicable to all linear chromatographic processes are rigorously developed.

The column efficiency should, in conjunction with the solvent efficiency, completely determine the overall efficiency. This requirement is not met if N is used as a measure of the column efficiency since it has been shown that the overall efficiency decreases as k is decreased[8], even though $N_1$, $N_2$ and $\alpha$ are kept constant. For this reason N should be replaced by a more suitable parameter. It is clear that this may best be done by obtaining an expression for the overall efficiency and by then defining the column efficiency in such a way that the overall efficiency is a function of the solute and column efficiencies only.

The most suitable approach at present available to the problem of the overall efficiency is via the impurity fraction treatment developed by Glueckauf[4], in which the extent to which a solute pair may be separated is described in terms of the degree of mutual contamination (impurity fractions) of the solute bands emerging from the column. He has shown that the impurity fractions of the two solutes depend on their molar ratio, which at first sight would seem to make the impurity fractions an unsuitable measure of the overall efficiency as the latter quantity should ideally not be dependent on the relative amounts of the solutes. However, this defect may be easily overcome by defining the overall efficiency as the impurity fractions of a *standard* molar ratio of the solutes—the most obvious choice being an equimolar ratio. Consider a chromatogram obtained by eluting an equimolar mixture of two solutes of negligible inlet volume. When the eluate portions are separated at $v = v_0$, the respective impurity fractions $\eta_1$ and $\eta_2$ are given[4] by

$$\eta_1 = \frac{\Delta M_2}{M_1 - \Delta M_1} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \quad (7)$$

$$\eta_2=\frac{\Delta M_1}{M_2-\Delta M_2} \qquad \ldots\ldots\ldots\ldots (8)$$

and, for $M_1=M_2$, the optimum cut may be determined by the condition that $\eta_1$ and $\eta_2$ should be equal, i.e.

$$\eta_1=\eta_2=\eta_{1:1} \qquad \ldots\ldots\ldots\ldots (9)$$

It is shown in equation (30) that $\eta_{1:1}$ is a function only of a parameter R, where

$$R=\frac{\bar{v}_2-\bar{v}_1}{\sigma_1+\sigma_2} \qquad \ldots\ldots\ldots\ldots (10)$$

From equations (1), (2), (5) and (10) it follows that

$$R=\frac{\alpha-1}{\left\{(1+k_1)/k_1\sqrt{N_1}\right\}+\alpha\left\{(1+k_2)/k_2\sqrt{N_2}\right\}} \qquad \ldots\ldots\ldots\ldots (11)$$

$\eta_{1:1}$ is determined by R, and the overall efficiency is thus a function of $\alpha$, $k_1^2N_1/(1+k_1)^2$ and $k_2^2N_2/(1+k_2)^2$. This result shows that, in order to express the overall efficiency as a function only of $\alpha$ and of the column efficiency, the parameter $k^2N/(1+k)^2$ should be used as a measure of the column efficiency in the place of N. From equations (2) and (5) it follows that

$$\frac{k^2N}{(1+k)^2}=\left(\frac{\bar{v}-v_g}{\sigma}\right)^2=16\left(\frac{\bar{v}-v_g}{w}\right)^2 \qquad \ldots\ldots\ldots\ldots (12)$$

It may be seen from equations (6) and (12) that $k^2N/(1+k)^2$ is equal to the factor S proposed by Purnell[8] as a measure of the column efficiency. The treatment followed by this author is, however, less general than our own, in that he considered only one value of the overall efficiency, (i.e. the value for which $(\bar{v}_2-\bar{v}_1)=3(\sigma_1+\sigma_2)$ ), and assumed that individual chromatograms possess an effective width of $6\sigma$ and that $\sigma_1=\sigma_2$.

The term "separation factor" proposed by Purnell[8] for the above measure of the column efficiency is ambiguous, as it is widely used [1, 2, 4] for the solvent efficiency $\alpha$. We propose the term *number of theoretical plates based on apparent retention*, denoted by $N_{BAR}$, and defined from equation (12) by

$$N_{BAR}=\left(\frac{\bar{v}-v_g}{\sigma}\right)^2=16\left(\frac{\bar{v}-v_g}{w}\right)^2 \qquad \ldots\ldots\ldots\ldots (13)$$

as the notation is unambiguous, and as it may be seen by comparing equations (5) and (13) that $N_{BAR}$ is determined in the same way as is N from the chromatogram, except that, to calculate $N_{BAR}$, the apparent retention volume $(\bar{v}-v_g)$ should be used, and not the retention volume $\bar{v}$. An added advantage of this notation is that it emphasises the relationship between $N_{BAR}$ and N, which become equivalent at large values of k in the same way as do equations (3) and (4).

A large amount of work has been concerned with the effect of the various column parameters on the column efficiency measured in terms of N[1]. The conclusions which have been made are valid provided that k is large. Even when k is small, the general trends which have been predicted for the relation between the column efficiency and those variables which do not determine k, e.g. eluate flow rate, are correct. Where, however, the effect on the column efficiency of a parameter determining k has been studied, e.g. the distribution coefficient of the solute between the stationary and mobile phases or the amount of the stationary phase, the results are frequently in error. For example, in gas-liquid chromatography the column efficiency, as measured by N, increases continuously[9] as the percentage of liquid phase is decreased at small values of k. When the column efficiency is measured by $N_{BAR}$, however, it is found that there is an optimum percentage of liquid phase[10] which should be used to obtain the greatest column efficiency.

For many purposes it has proved convenient to define a measure of the column efficiency which is in most cases independent of the column length, and the height equivalent per theoretical plate[11]

$$H=\frac{L}{N} \qquad \ldots\ldots (14)$$

has been extensively used in this connection. For reasons similar to those given above we propose that H be replaced by the *height equivalent per theoretical plate based on apparent retention*, defined by

$$H_{BAR}=\frac{L}{N_{BAR}} \qquad \ldots\ldots (15)$$

$H_{BAR}$ may be simply related to H as follows:
From equations (12) and (13),

$$N_{BAR}=\frac{k^2N}{(1+k)^2} \qquad \ldots\ldots (16)$$

and by using equations (14) and (15), $H_{BAR}$ is then given by

$$H_{BAR}=\frac{(1+k)^2H}{k^2} \qquad \ldots\ldots (17)$$

By means of equation (17), the results of a large number of rate theories of chromatography,[11, 12, 13] which are given as expressions for H, may easily be written in terms of $H_{BAR}$.

Although the impurity fraction $\eta_{1:1}$ has been used in the foregoing discussion to describe the overall efficiency it is not in all respects entirely satisfactory in practice. Firstly impurity fractions cannot easily be determined directly from the chromatogram; secondly they are complicated functions of $(N_{BAR})_1$, $(N_{BAR})_2$ and $\alpha$; thirdly they vary over an inconveniently wide range in practice (for example in Fig. 2 it may be seen that a relatively small change in the overlapping of the peaks is accompanied by a large relative change in $\eta_{1:1}$).

These disadvantages are eliminated by employing the parameter R (equation (10) ), which is a function of $\eta_{1:1}$ only (equation (31) ), to measure the overall efficiency. We propose that R be termed the *peak resolution* of the two solutes 1 and 2.

By comparing equations (5) and (10) it may be seen that

$$R=4\left(\frac{\bar{v}_2-\bar{v}_1}{w_1+w_2}\right) \quad \ldots \tag{18}$$

which should be regarded as the definition of the peak resolution. Equation (18) clearly shows that R increases as the volume $(\bar{v}_2-\bar{v}_1)$ between the peak maxima is increased, and also increases as the band widths are decreased. Several advantages accrue from the use of R, as distinct from $\eta_{1:1}$, as a measure of the overall efficiency. R is readily determined from the chromatogram, and in fact, as only the difference $(\bar{v}_2-\bar{v}_1)$ is needed, the point at which the solutes are introduced need not be known. The desirability of a simple relation between the overall efficiency, and $(N_{\text{BAR}})_1$, $(N_{\text{BAR}})_2$ and $\alpha$, has been pointed out above. This requirement is met by the definition of R given here, since it follows from equations (11) and (16) that when $(N_{\text{BAR}})_1=(N_{\text{BAR}})_2=\overline{N_{\text{BAR}}}$,

$$R^2=\left(\frac{\alpha-1}{\alpha+1}\right)^2\overline{N_{\text{BAR}}} \quad \ldots \tag{19}$$

When $(N_{\text{BAR}})_1$ is not equal to $(N_{\text{BAR}})_2$, $\overline{N_{\text{BAR}}}$ may be regarded as an average value. This point is discussed more fully below. From the values of R and $\eta_{1:1}$ in Fig. 2 it may be seen that in practice the overall efficiency is more conveniently described in terms of the value of R than of the value of $\eta_{1:1}$.

It is interesting to note that equation (18) corresponds closely to the preliminary expression[14] $2\left(\frac{\bar{v}_2-\bar{v}_1}{w_1+w_2}\right)$ proposed on *empirical grounds* by the nomenclature committee of the Gas Chromatography Discussion Group. The simplicity of equations (19) and (31) leads us to prefer R to R/2, or any other multiple of R, as a measure of the overall efficiency.

For the same reasons that have been given for the introduction of $H_{\text{BAR}}$, it is convenient to define a measure of the overall efficiency, which, in most cases, will be independent of the column length, as

$$\Gamma=\frac{L}{R^2} \quad \ldots \tag{20}$$

$\Gamma$ is the length of the column required to give a peak resolution of $R=1$, and is given from equations (15), (19) and (20) by

$$\Gamma=\left(\frac{\alpha+1}{\alpha-1}\right)^2\overline{H_{\text{BAR}}} \quad \ldots \tag{21}$$

When studies are being carried out to determine the optimum column conditions which should be used in order to effect the best possible separations, the following considerations should be taken into account. Where parameters other than those affecting $\alpha$ are being varied, e.g. where the effect of the eluate flow rate is being investigated, the variation of $N_{\text{BAR}}$ or $H_{\text{BAR}}$ should be followed, as the latter quantities may be determined from the elution curve of one solute only. If any parameter affecting $\alpha$, e.g. the stationary phase or the column temperature, is varied, the variation in R or Γ should be followed. Even when $\alpha$ varies continuously during a run, as in temperature programming, R, as defined by equation (18), remains a valid measure of the overall efficiency. This also applies to all other relations in this paper which do not involve $\alpha$ or $N_{BAR}$.

*Efficiency requirements for analytical separations by linear chromatography*

The object of analytical chromatography is to identify and estimate each of the components of a solute mixture. This is done[1] either directly from the chromatogram, by determining the positions of the elution peak maxima relative to the injection point and by measuring the peak areas, or by eluting the eluate in fractions and employing an auxillary method of analysing the fractions (e.g. mass spectrometry). In order to obtain accurate results by either of these methods the extent to which the solutes are separated should be as great as possible, i.e. the overlap of the elution curves, and thus the impurity fractions, should be as small as possible. The solute volume at the column inlet should therefore be sufficiently small[11] not to cause a noticeable increase in the widths of the elution bands at the column outlet.

In the present study we shall determine the values of the overall efficiency and of the column efficiency required to separate two solutes to different extents. Both the simplest case where the molar ratio of the solutes is unity and the case where the molar ratio may assume any value will be considered.

The concentration of a solute in the mobile phase at the column exit is given[11], under the assumptions that the distribution isotherm is linear and that the inlet volume of the solute is negligible, by the Gaussian function

$$\mathrm{c}=\frac{\mathrm{M}}{\sqrt{2\pi\sigma^2}}\exp\left\{-\frac{(v-\bar{v})^2}{2\sigma^2}\right\} \quad \ldots \ldots \ldots \ldots \ldots \ldots (22)$$

When two solutes are eluted and appear at the column exit with concentrations $c_1$ and $c_2$, in that order, the eluate may be cut at a point $v=v_0$ between the peaks. The minor portion of the first solute is then given by

$$\Delta \mathrm{M}_1=\int_{v_0}^{\infty}\mathrm{c}_1\,\mathrm{d}v \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (23)$$

Let

$$\mathrm{A(X)}=\int_{-\infty}^{\mathrm{X}}\frac{1}{\sqrt{2\pi}}\exp\left\{-\frac{\mathrm{t}^2}{2}\right\}\mathrm{dt} \quad \ldots \ldots \ldots \ldots \ldots \ldots (24)$$

denote the integral of the probability function.
From equations (22), (23) and (24),

$$\Delta \mathrm{M}_1=\mathrm{M}_1(1-\mathrm{A}[(v_0-\bar{v}_1)/\sigma_1]) \quad \ldots \ldots \ldots \ldots \ldots \ldots (25)$$

Similarly,

$$\Delta \mathrm{M}_2=\mathrm{M}_2(1-\mathrm{A}[(\bar{v}_2-v_0)/\sigma_2]) \quad \ldots \ldots \ldots \ldots \ldots \ldots (26)$$

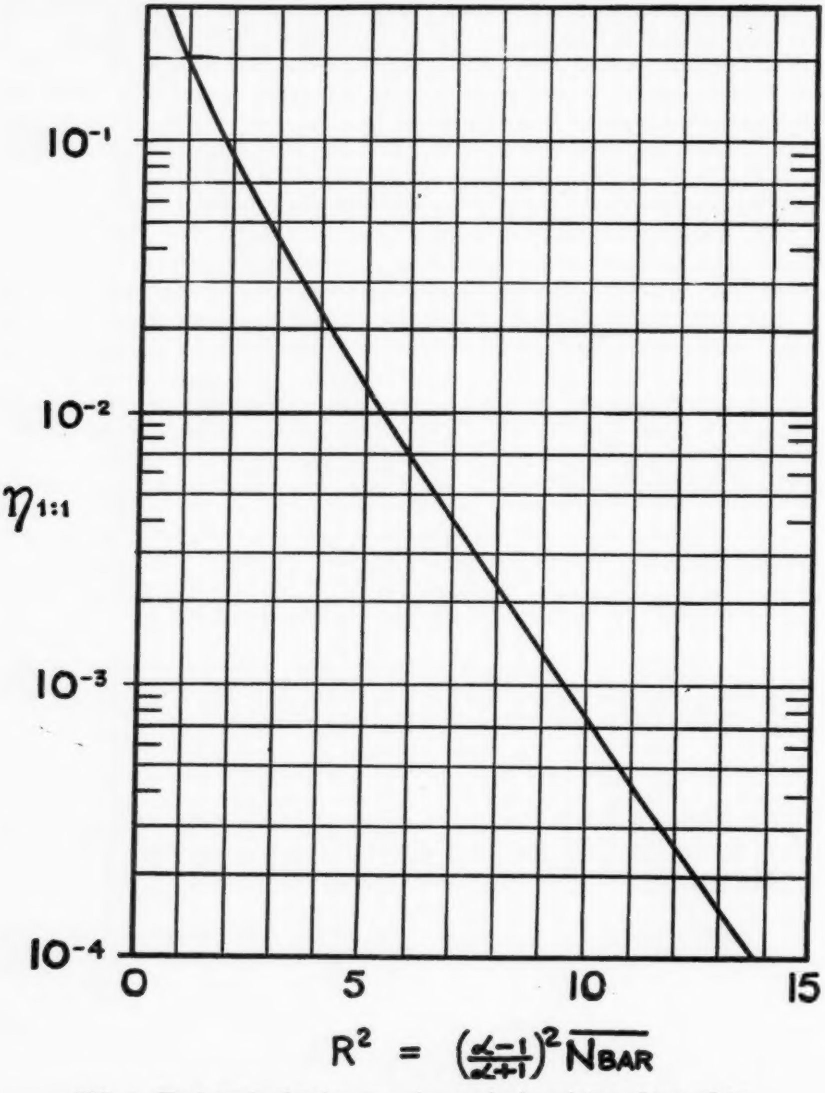

FIG. 1—The impurity fraction $\eta_{1:1}$ of an equimolar mixture of two solutes, calculated from equation (31) for various values of the peak resolution R.

$\eta_1$ and $\eta_2$ are given, from equations (7), (8), (25) and (26) by

$$\eta_1 = \frac{M_2(1 - A[(\bar{v}_2 - v_0)/\sigma_2])}{M_1 A[(v_0 - \bar{v}_1)/\sigma_1]} \quad \ldots \ldots \ldots \ldots \ldots \ldots (27)$$

$$\eta_2 = \frac{M_1(1 - A[(v_0 - \bar{v}_1)/\sigma_1])}{M_2 A[(\bar{v}_2 - v_0)/\sigma_2]} \quad \ldots \ldots \ldots \ldots \ldots \ldots (28)$$

Consider firstly the elution of an equimolar mixture of two solutes. The optimum cut $v_0$, which determines $\eta_{1:1}$, is then given from equations (9), (27) and (28) by

$$\frac{v_0 - \bar{v}_1}{\sigma_1} = \frac{\bar{v}_2 - v_0}{\sigma_2} = \frac{\bar{v}_2 - \bar{v}_1}{\sigma_1 + \sigma_2} \quad \ldots \ldots \ldots \ldots \ldots \ldots (29)$$

The optimum cut $v_0$ is thus determined by the condition that the distances $(v_0 - \bar{v}_1)$ and $(\bar{v}_2 - v_0)$ to the peak maxima should be proportional to the band widths $w_1 = 4\sigma_1$ and $w_2 = 4\sigma_2$. $\eta_{1:1}$ is given from equations (9), (27) and (29) by

$$\eta_{1:1} = \frac{1 - A\left(\dfrac{\bar{v}_2 - \bar{v}_1}{\sigma_1 + \sigma_2}\right)}{A\left(\dfrac{\bar{v}_2 - \bar{v}_1}{\sigma_1 + \sigma_2}\right)} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (30)$$

and $\eta_{1:1}$ may thus be written in terms of R (equation (10) ):

$$\eta_{1:1} = \frac{1 - A(R)}{A(R)} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (31)$$

In Fig. 1, a graph is given of $\eta_{1:1}$ for various values of $R^2 = \left(\frac{\alpha - 1}{\alpha + 1}\right)^2 \overline{N_{BAR}}$ (equation (19) ). This curve may be used to calculate the purity with which two solutes in an equimolar mixture may be separated for a given value of R.

The chromatograms in Fig. 2 illustrate the extent to which two solutes in an equimolar mixture are separated at various values of the overall efficiency. For each chromatogram, the sum $(c_1 + c_2)$ of the solute concentrations has been calculated from equations (10) and (22) as a function of the volume $v$ of the eluting solution. The solid and dashed lines indicate the retention volumes $\bar{v}_1$ and $\bar{v}_2$, and the optimum cut volume $v_0$, respectively. The minor fractions $\Delta M_1$ and $\Delta M_2$ are indicated by the blacked portions. In the chromatograms on the left, the band widths of the two component curves are equal, i.e. $\sigma_1 = \sigma_2$. This is normally approximately true in practice. The corresponding curves for $2\sigma_1 = \sigma_2$ are also given in order to assess the influence of the ratio $\sigma_2/\sigma_1$ on the extent of separation. The results in Fig. 2 show clearly that the extent to which two solutes in an equimolar mixture are separated is satisfactorily described by the overall efficiency, and that the ratio of the band widths of the peaks is of less importance. For all practical purposes, peak overlapping is negligible when $R \geqslant 3$. As R becomes smaller, peak overlapping increases, and the depth of the minimum between the peaks decreases, until, for $\sigma_1 = \sigma_2$, it finally becomes zero at $R = 1$, as may easily be shown by differentiation.

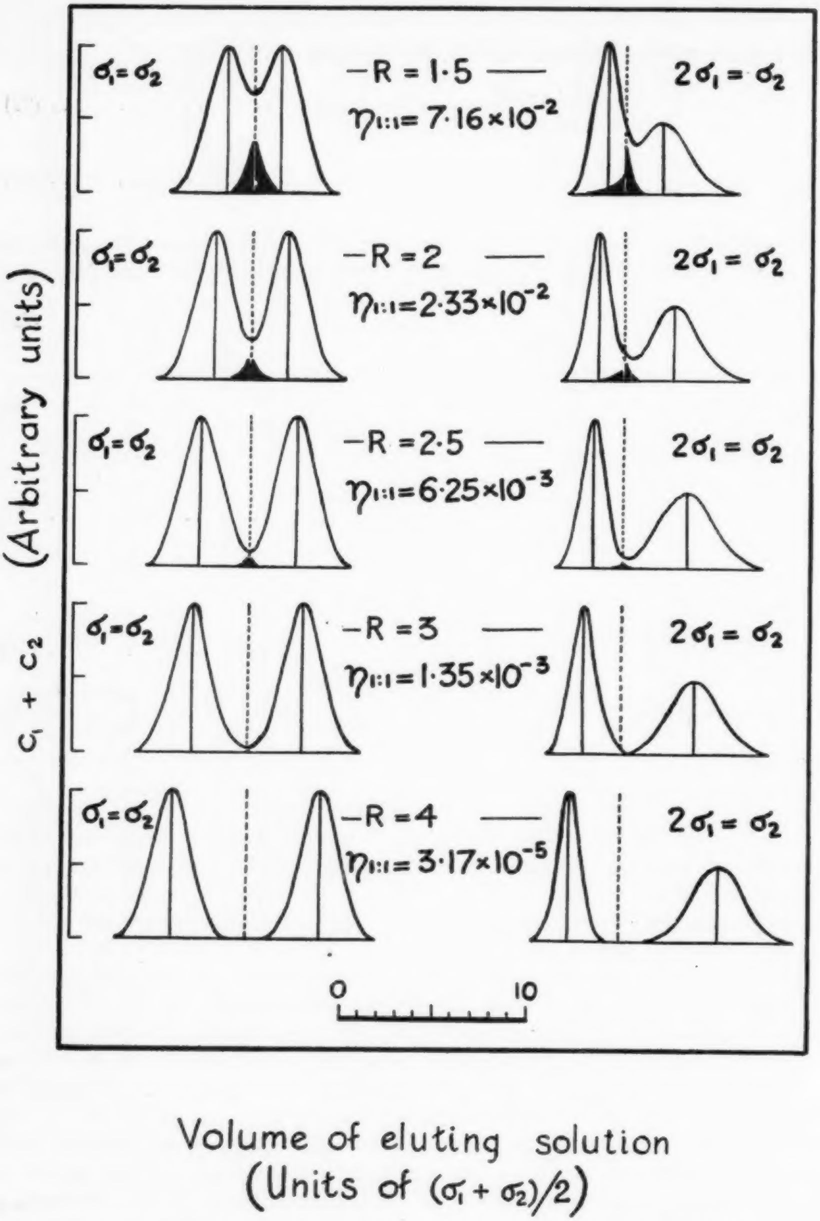

FIG. 2—Chromatograms illustrating the extent to which two solutes in an equimolar mixture are separated at various values of the overall efficiency. For each chromatogram, the sum $(c_1+c_2)$ of the solute concentrations has been calculated from equations (10) and (22) as a function of the volume of the eluting solution. The solid and dashed lines indicate the retention volumes $\overline{v_1}$ and $\overline{v_2}$, and the optimum cut volume $v_0$, respectively. The minor fractions $\Delta M_1$ and $\Delta M_2$ are indicated by the blacked portions.

The extent to which two solutes in an equimolar mixture must be separated in order to carry out a quantitative analysis may be specified by a minimum required value, $R_{1:1}$, of R. The corresponding minimum required value of the column efficiency, $(\overline{N_{BAR}})_{1:1}$, is then given by

$$(\overline{N_{BAR}})_{1:1}=R^2_{1:1}\left(\frac{\alpha+1}{\alpha-1}\right)^2 \quad \ldots \quad (32)$$

which follows from equation (19). In Fig. 3, $(\overline{N_{BAR}})_{1:1}$ has been plotted against $\alpha$ for various values of $R_{1:1}$. These graphs may be used to determine the column efficiency required for the analysis of an equimolar solute mixture. The value of $(\overline{N_{BAR}})_{1:1}$ is proportional to $R^2_{1:1}$ at constant $\alpha$, and it thus increases very rapidly with $R_{1:1}$. It is therefore most important that a careful decision should be made as to the smallest value of $R_{1:1}$ with which a satisfactory analysis may be obtained; in fact, modern computing methods[15] should make it possible to analyse a chromatogram where R is so small that the individual peaks may no longer be distinguished. It is for these reasons that we feel that $R_{1:1}$ should be treated as a variable parameter. van Deemter *et al.*[11] and Purnell[8] have employed fixed values of the minimum overall efficiency required for analytical purposes. By comparing their equations with those given in the present paper, it may be seen that they have chosen the values $R_{1:1}=2$ and $R_{1:1}=3$ respectively. The disadvantages of these proposals should now be apparent.

Consider now the elution of a non-equimolar mixture of two solutes. Let m and p respectively denote the molar and the band width ratio of the smaller peak to the larger peak. (p may be found in terms of $(N_{BAR})_1$, $(N_{BAR})_2$ and $\alpha$, as

$$\frac{\sigma_2}{\sigma_1}=\alpha\sqrt{\frac{(\overline{N_{BAR}})_1}{(\overline{N_{BAR}})_2}} \quad \ldots \quad (33)$$

from equations (3) and (13)). It may be assumed without any loss of generality that $M_2 \leqslant M_1$, i.e. that

$$m=\frac{M_2}{M_1} \quad \ldots \quad (34)$$

and that

$$p=\frac{\sigma_2}{\sigma_1} \quad \ldots \quad (35)$$

Glueckauf[4] has described the extent to which the solutes in a non-equimolar mixture are separated, by means of an impurity fraction $\overline{\eta_m}$ which is found by choosing the cut volume $v_0$ in such a way that

$$\eta_1=\eta_2=\overline{\eta_m} \quad \ldots \quad (36)$$

We define an alternative impurity fraction $\eta_m$ as the impurity fraction of the smaller peak at a cut volume $v_0$ for which

$$\Delta M_1=\Delta M_2 \quad \ldots \quad (37)$$

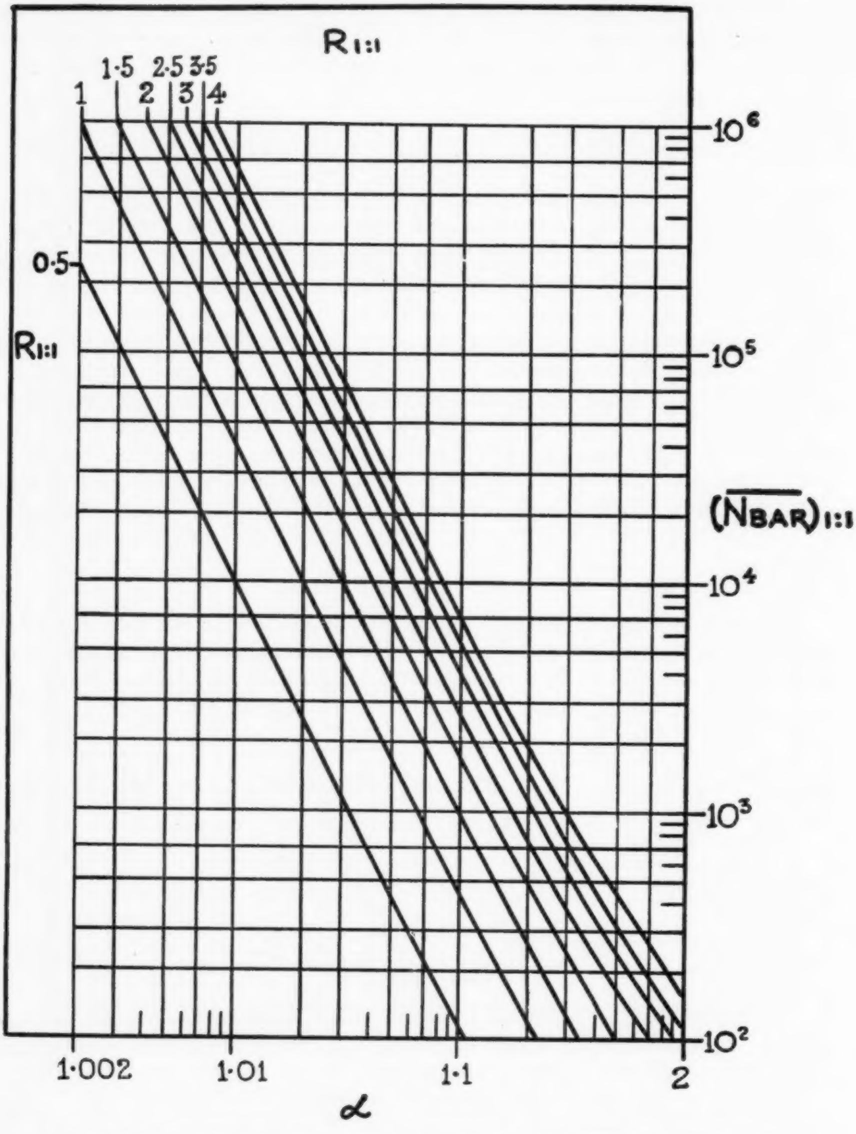

FIG. 3—The minimum value of the column efficiency, $(\overline{N_{BAR}})_{1:1}$, required for the separation of an equimolar mixture. $(\overline{N_{BAR}})_{1:1}$ has been calculated from equation (32) as a function of the separation factor $\alpha$, for various specified values, $R_{1:1}$, of the peak resolution R.

Let

$$x=\frac{v_0-\bar{v}_1}{\sigma_1} \quad \text{.. .. .. .. .. .. .. .. ..} \quad (38)$$

By using equations (10), (34), (35) and (38), it follows from equations (27), (28) and (36) that $\overline{\eta_m}$ may be found by solving the equation

$$\overline{\eta_m}=\frac{m\left[1-A\left\{\frac{(1+p)R-x}{p}\right\}\right]}{A(x)}=\frac{1-A(x)}{mA\left\{\frac{(1+p)R-x}{p}\right\}} \quad \text{.. .. ..} \quad (39)$$

for x, and from equations (25), (26), (28) and (37) that $\eta_m$ is given by

$$\eta_m=\frac{1-A\left\{\frac{(1+p)R-x}{p}\right\}}{A\left\{\frac{(1+p)R-x}{p}\right\}} \quad \text{.. .. .. .. .. .. ..} \quad (40)$$

where x is the solution of the equation

$$1-A(x)=m\left[1-A\left\{\frac{(1+p)R-x}{p}\right\}\right] \quad \text{.. .. .. .. .. ..} \quad (41)$$

The precise relationship between $\eta_m$, $\overline{\eta_m}$, R, p and m will be complex. Approximate formulae may, however, be derived for large values of R. It is shown in the appendix that

$$\overline{\eta_m} \xrightarrow[\infty]{R} m^{(p-1)/(p+1)}\eta_{1:1} \quad \text{.. .. .. .. .. .. ..} \quad (42)$$

where the solution of equation (39) is

$$x \xrightarrow[\infty]{R} R+\frac{2p}{(1+p)R}\ln\left(\frac{1}{m}\right) \quad \text{.. .. .. .. .. .. .. ..} \quad (43)$$

Similarly, it may be shown that

$$\eta_m \xrightarrow[\infty]{R} m^{-1/(1+p)}\eta_{1:1} \quad \text{.. .. .. .. .. .. .. ..} \quad (44)$$

where the solution of equation (41) is given by

$$x \xrightarrow[\infty]{R} R+\frac{p}{(1+p)R}\ln\left(\frac{1}{m}\right) \quad \text{.. .. .. .. .. .. .. ..} \quad (45)$$

An equation corresponding to equation (42) has been derived by Glueckauf[4], i.e.

$$\overline{\eta_m} \xrightarrow[\infty]{R} \frac{2m}{1+m^2}\eta_{1:1} \quad \text{.. .. .. .. .. .. .. .. ..} \quad (46)$$

In Fig. 4, $\eta_m/\eta_{1:1}$ and $\overline{\eta_m}/\eta_{1:1}$ have been plotted against m for various values of R. For convenience a value p=1 has been chosen. $\eta_m$, $\overline{\eta_m}$ and $\eta_{1:1}$ have been calculated for finite values of R from equations (31), (39), (40) and (41). For R=∞ and p=1, equations (42) and (44) yield $\overline{\eta_m}/\eta_{1:1}=1$ and $\eta_m/\eta_{1:1}=1/\sqrt{m}$, respectively. The latter

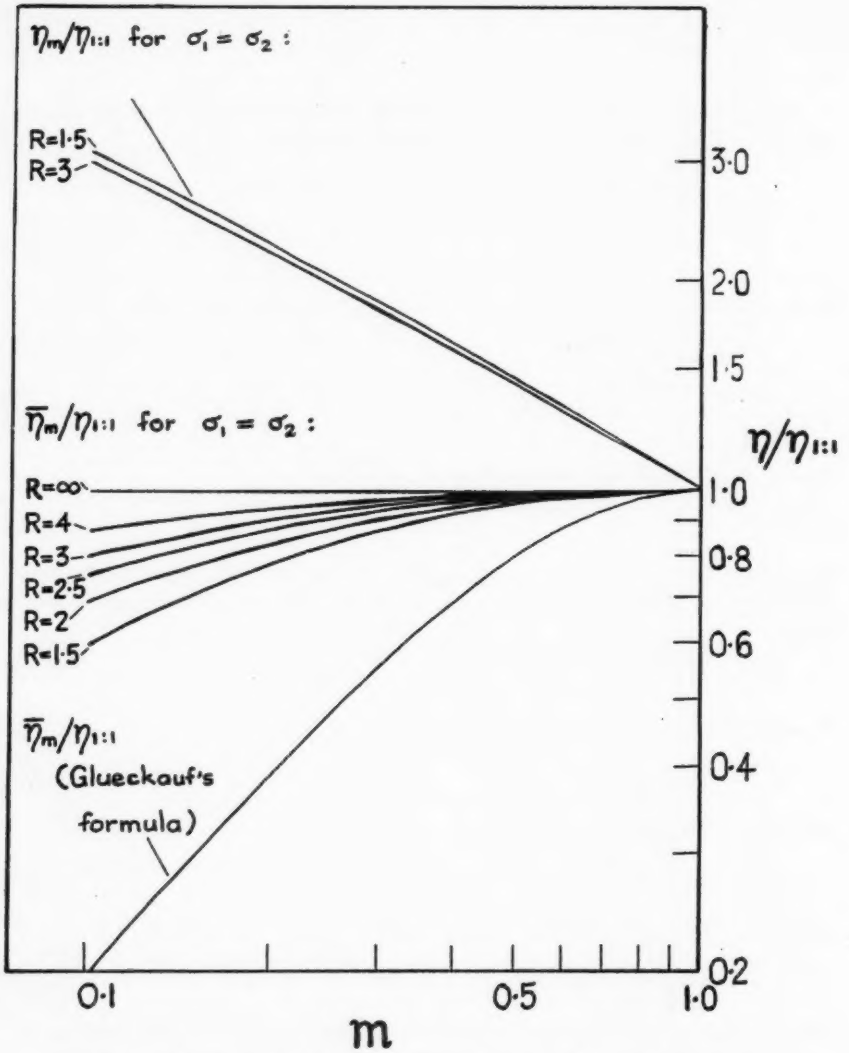

FIG. 4—The influence of the molar ratio m of the smaller to the larger peak on the impurity fractions $\eta_m$ and $\overline{\eta_m}$. Peaks of equal width have been considered. $\eta_m/\eta_{1:1}$ and $\overline{\eta_m}/\eta_{1:1}$ have been calculated from equations (31), (39), (40), (41) and (42). $\overline{\eta_m}/\eta_{1:1}$, as determined from equation (46), has also been plotted against m.

relation has not been plotted in Fig. 4, as the curve coincides to a large extent with those found for $\eta_m/\eta_{1:1}$ at $R=1{\cdot}5$ and $R=3$. In the same figure, $\overline{\eta_m}/\eta_{1:1}$, as determined from equation (46), has also been plotted against m. From the results in Fig. 4 it may be seen that for $p=1$, $\overline{\eta_m}/\eta_{1:1} \xrightarrow[\infty]{R} 1$, which is in agreement with equation (42). The equation derived by Glueckauf for large values of R (equation (46) ) is incorrect. The reason for the discrepancy between equations (42) and (46) lies in the unjustified approximations made in the Taylor-series expansions used by Glueckauf in the derivation of equation (46). Furthermore, equation (46) has been extensively used [16,17] in practice to calculate $\overline{\eta_m}/\eta_{1:1}$ for all values of R and of p. It may, however, be seen from Fig. 4 that $\overline{\eta_m}/\eta_{1:1}$ varies significantly as R is varied, and that the indiscriminate use of a relation valid for $R=\infty$ to calculate impurity fractions for small values of R may lead to erroneous results. As a result of the definitions of the impurity fractions, $\eta_m$ and $\overline{\eta_m}$, $\eta_m$ increases but $\overline{\eta_m}$ decreases when m is made smaller. According to equation (44), $\eta_m/\eta_{1:1}=1/\sqrt{m}$ for $p=1$ and large values of R. This relation is also found to hold well for relatively small R values, e.g. for $p=1$ and $m=0{\cdot}1$, $\eta_m/\eta_{1:1}=3{\cdot}162$, $2{\cdot}995$ and $3{\cdot}109$ for $R=\infty$, 3 and $1{\cdot}5$, respectively.

The chromatograms in Fig. 5 illustrate the extent to which two solutes are separated at various values of m, R, $\overline{\eta_m}$ and $\eta_m$, for $p=1$, i.e. $\sigma_1=\sigma_2$. The conventions followed are similar to these followed in Fig. 2. In the chromatograms on the left side of the figure, R is kept constant at $R=2$, with the result that $\overline{\eta_m}$, calculated from equation (39), decreases as m is decreased. In those on the right, $\eta$ is kept constant at the value of $\eta_{1:1}$ for $R=2$, (i.e. at $\eta_m=0{\cdot}0233$), by increasing R as m is decreased. This may be done by means of equation (51).

It may be seen from Fig. 5 that, when m is not equal to 1, the area of the smaller peak cannot be determined as accurately as can that of the larger peak. The accuracy of the analysis, as measured by the percentage error made in the determination of each solute, thus depends on the extent to which the smaller peak is separated from the larger peak. When m is decreased at constant R, the smaller peak becomes swamped by the larger one, even though $\overline{\eta_m}$ is decreased. If $\overline{\eta_m}$ had been kept constant by decreasing R as m was decreased, this effect would have been even more apparent. When $\eta_m$ is kept constant by increasing R as m is decreased, the smaller peak remains separated from the larger one to much the same degree. Consequently, $\eta_m$, and not $\overline{\eta_m}$, should be used to describe the extent to which the two solutes are separated. Furthermore, the minimum values of the overall and column efficiencies required for a quantitative analysis will increase as m is decreased. This result is in disagreement with Glueckauf's theory[4], which states that the minimum required value of the column efficiency decreases as m is made smaller.

It should be noted that the concept of the extent of separation of two solutes has until now been developed in terms of molar impurity fractions. From Fig. 5 it now becomes clear that the extent of separation is in practice intimately connected

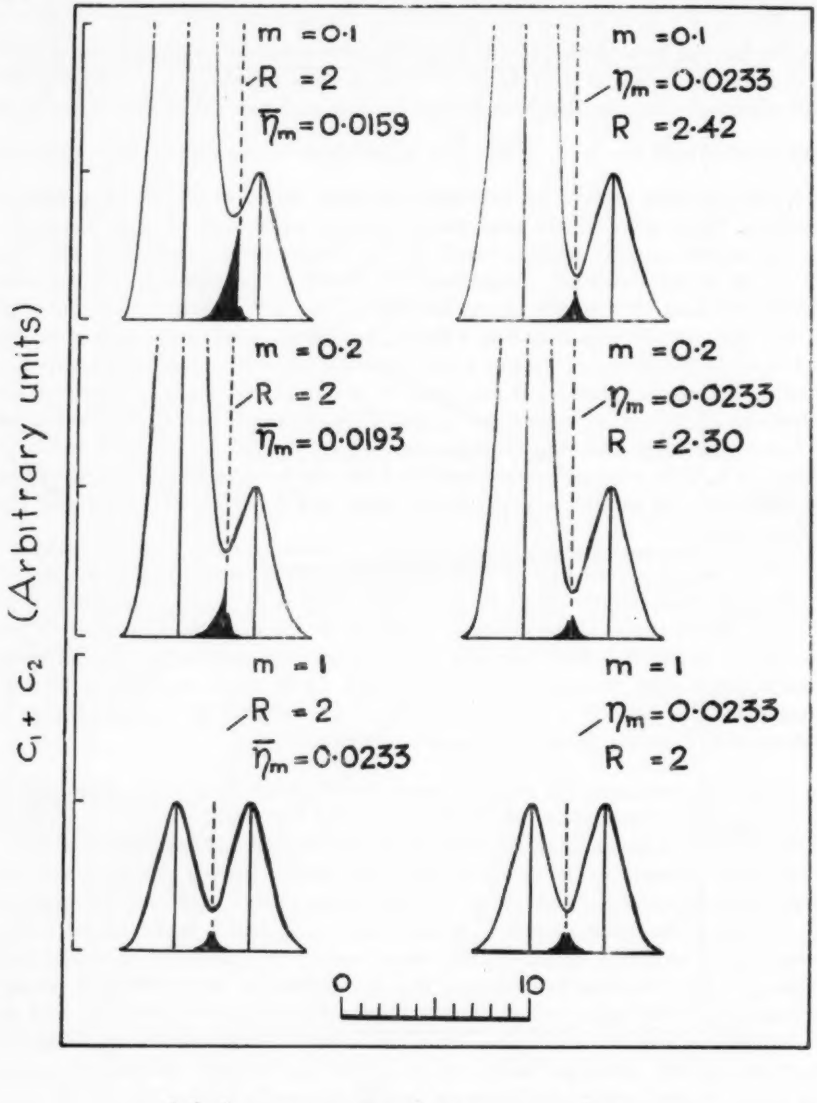

FIG. 5—Chromatograms illustrating the extent to which peaks of equal width are separated at various values of m, R$\overline{\eta}_m$, and $\eta_m$. The conventions followed are similar to those followed in Fig. 2. $\overline{\eta}_m$ has been calculated, for R=2, from equation (39), while R has been calculated, for $\eta_m$= 0.0233, from equation (51).

with the geometry of the recorded detector deflection, and in particular with the relative areas of the individual elution peaks. For the sake of brevity we have assumed that the detector response per unit concentration of the two solutes is the same, i.e. that an equimolar mixture of the solutes will produce recorded peaks of the same area. Where this is not true a correction may readily be made, by replacing $M_2$ by $\gamma M_2$, where $\gamma$ is the ratio of the detector response for the solute 2 to that of the solute 1, at equal concentrations.

The minimum value, $R_m$, of the overall efficiency required for a quantitative analysis may be determined as follows. Let $\eta_m$ and $\eta_{1:1}$.respectively designate the impurity fractions corresponding to $R=R_m$ when $M_1$ is not equal to $M_2$ and to $R=R_{1:1}$ when $M_1=M_2$. As $\eta_m$ describes the extent to which the two solutes are separated, it follows that

$$\eta_m=\eta_{1:1} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (47)$$

$R_m$ is determined from equations (31), (40) and (47) by the condition

$$\frac{(1+p)R_m-x}{p}=R_{1:1} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (48)$$

where x is the solution of equation (41) for $R=R_m$. From equations (41) and (48),

$$1-A(x)=m[1-A(R_{1:1})] \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (49)$$

Let X (A) designate the value of X for which the probability integral (equation (24) ) has the value A. x is then given by

$$x=X[1-m(1-A(R_{1:1}))] \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (50)$$

$R_m$ may now be found by eliminating x from equations (48) and (50), viz.

$$R_m=\frac{X[1-m(1-A(R_{1:1}))]+pR_{1:1}}{1+p} \quad \ldots \ldots \ldots \ldots \ldots (51)$$

The minimum required value, $(\overline{N_{BAR}})_m$, of the column efficiency is given from equations (19) and (32) by

$$\frac{(\overline{N_{BAR}})_m}{(\overline{N_{BAR}})_{1:1}}=\frac{R_m^2}{R_{1:1}^2} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (52)$$

In Fig. 6, the latter quantities have been plotted against m for various values of p and of $R_{1:1}$. $R_m$ has been calculated from equation (51). The results in Fig. 6 may be used in conjunction with those in Figs. 1 and 3, to determine the values of R and of $\overline{N_{BAR}}$ required for analyses.

### *The average column efficiency*

When $(N_{BAR})_1$ is not equal to $(N_{BAR})_2$, the average column efficiency, $\overline{N_{BAR}}$, with which the two solutes are separated may best be defined by means of equation (19). It then follows from equations (11), (16) and (19) that

$$\overline{N_{BAR}}=\left[\frac{\alpha+1}{1/\sqrt{(N_{BAR})_1}+\alpha/\sqrt{(N_{BAR})_2}}\right]^2 \quad \ldots \ldots \ldots \ldots \ldots (53)$$

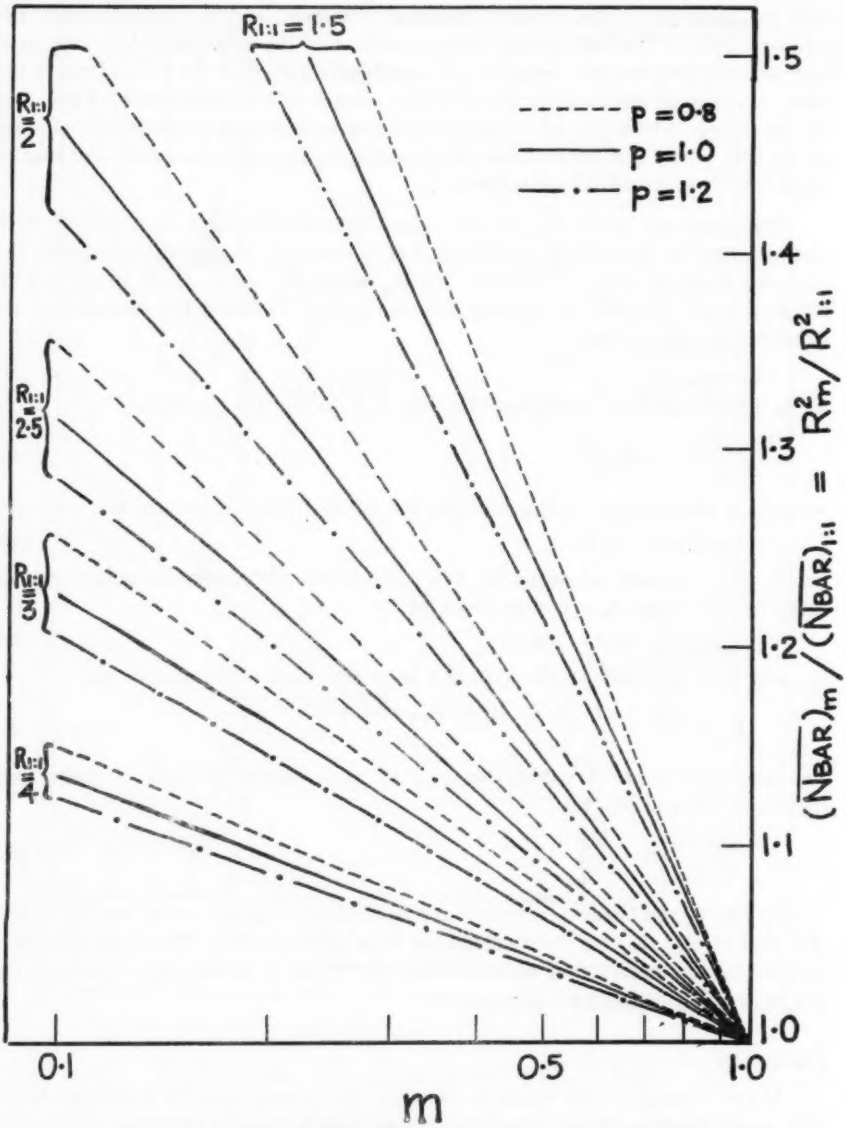

FIG. 6—The influence of the molar ratio, m, of the smaller peak to the larger peak, on the efficiency requirements for analyses. The required minimum values, $R_m$ and $(\overline{N_{BAR}})_m$, of the overall and column efficiencies, respectively, have been calculated from equations (51) and (52) for various values of p.

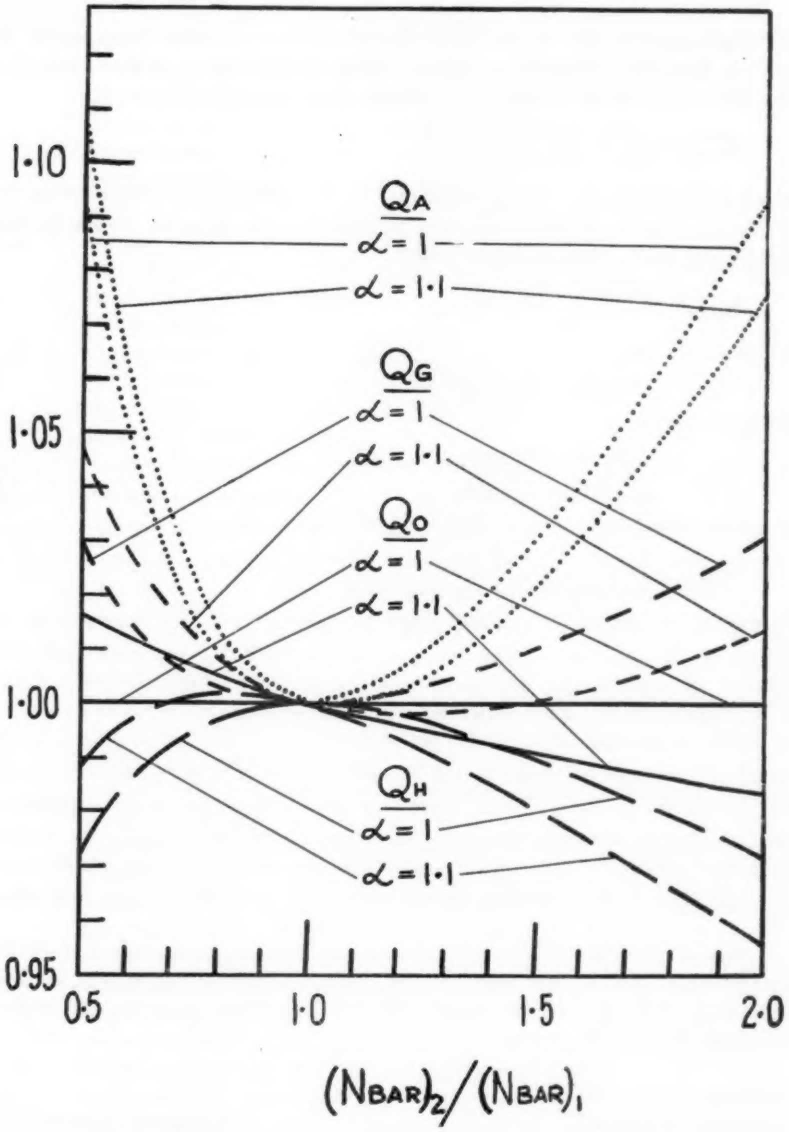

FIG. 7—$Q_A$, $Q_G$, $Q_H$ and $Q_O$ respectively indicate the ratios of the approximate mean values $\overline{N_{BAR}}^A$, $\overline{N_{BAR}}^G$, $\overline{N_{BAR}}^H$ and $\overline{N_{BAR}}^O$, of $(N_{BAR})_1$ and $(N_{BAR})_2$, to the true mean value $\overline{N_{BAR}}$. These ratios have been calculated from equations (53), (55), (56), (57) and (58) for various values of $\alpha$ and of $(N_{BAR})_2/(N_{BAR})_1$.

Although equation (53) at first sight appears to be somewhat cumbersome, $\overline{N_{BAR}}$ may, in fact, be determined as easily from a chromatogram as may $(N_{BAR})_1$ and $(N_{BAR})_2$: by substituting equations (3) and (13) in equation (53), we find

$$\overline{N_{BAR}}=16\left(\frac{(\bar{v}_1-v_g)+(\bar{v}_2-v_g)}{w_1+w_2}\right)^2 \quad \ldots \quad (54)$$

which is similar in form to equation (13). In calculating $\overline{N_{BAR}}$ from existing values of $(N_{BAR})_1$, $(N_{BAR})_2$ and $a$, $\overline{N_{BAR}}$ may be approximated by mean values of $(N_{BAR})_1$ and $(N_{BAR})_2$ such as the arithmetic mean

$$\overline{N_{BAR}}^{A}=\frac{(N_{BAR})_1+(N_{BAR})_2}{2} \quad \ldots \quad (55)$$

the geometric mean

$$\overline{N_{BAR}}^{G}=[(N_{BAR})_1\cdot(N_{BAR})_2]^{1/2} \quad \ldots \quad (56)$$

the harmonic mean

$$\overline{N_{BAR}}^{H}=\frac{2(N_{BAR})_1\cdot(N_{BAR})_2}{(N_{BAR})_1+(N_{BAR})_2} \quad \ldots \quad (57)$$

or a mean value derived by putting $a=1$ in equation (53),

$$\overline{N_{BAR}}^{O}=\left[\frac{2}{1/\sqrt{(N_{BAR})_1}+1/\sqrt{(N_{BAR})_2}}\right]^2 \quad \ldots \quad (58)$$

In Fig. 7, the respective ratios $Q_A$, $Q_G$, $Q_H$, and $Q_O$ of these approximate mean values, to the true mean value $\overline{N_{BAR}}$ of $(N_{BAR})_1$ and $(N_{BAR})_2$, have been plotted against $(N_{BAR})_2/(N_{BAR})_1$ for $a=1$ and for $a=1{\cdot}1$. It may be seen that, for $0{\cdot}7\leqslant(N_{BAR})_2/(N_{BAR})_1\leqslant 1{\cdot}5$, all the averaging processes approach the true mean value to within approximately 3%. In practice, the value of $(N_{BAR})_2/(N_{BAR})_1$ should usually lie between 0·7 and 1·5, and $\overline{N_{BAR}}$ may then be approximated most simply by the arithmetic mean, $\overline{N_{BAR}}^{A}$ (equation (55) ). When $(a-1)\ll 1$, equation (58) may be used to determine $\overline{N_{BAR}}$ for all values of $(N_{BAR})_2/(N_{BAR})_1$. By comparing equations (15) and (57) it may be seen that the harmonic mean of $(N_{BAR})_1$ and $(N_{BAR})_2$, $\overline{N_{BAR}}^{H}$, is equivalent to the arithmetic mean of $(H_{BAR})_1$ and $(H_{BAR})_2$.

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## LIST OF SYMBOLS

| | |
|---|---|
| 1 | subscript designating the more weakly retarded solute of a pair |
| 2 | subscript designating the more strongly retarded solute of a pair |
| A | integral of the probability function |
| c | concentration of a solute in the eluate at the column exit |
| H | height equivalent per theoretical plate |
| $H_{BAR}$ | height equivalent per theoretical plate based on apparent retention |
| $\overline{H_{BAR}}$ | average value of $(H_{BAR})_1$ and $(H_{BAR})_2$ |
| k | ratio of the mass of a solute in the stationary phase to the mass in the mobile phase, at equilibrium |
| L | column length |
| M | total amount of the solute (moles) |
| $\Delta M$ | minor portion of the solute at a cut volume $v_0$ (moles) |
| m | molar ratio of the smaller to the larger peak |
| N | number of theoretical plates |
| $N_{BAR}$ | number of theoretical plates based on apparent retention |
| $\overline{N_{BAR}}$ | average column efficiency for the separation of the solutes 1 and 2 |
| $(\overline{N_{BAR}})_{1:1}$ | column efficiency required for the separation of an equimolar mixture |
| $(\overline{N_{BAR}})_m$ | column efficiency required for the separation of a non-equimolar mixture |
| p | ratio of the width of the smaller peak to that of the larger peak |
| Q | ratio of various approximate mean values of $(N_{BAR})_1$ and $(N_{BAR})_2$ to the true mean value $\overline{N_{BAR}}$ |
| R | peak resolution |
| $R_{1:1}$ | overall efficiency required for the separation of an equimolar mixture |
| $R_m$ | overall efficiency required for the separation of a non-equimolar mixture |
| S | convenient symbol ($S=N_{BAR}$) |
| $v$ | volume of the eluate as measured from the injection of the solute mixture |
| $\bar{v}$ | retention volume |
| $v_g'$ | retention volume for a solute which is not retarded by the stationary phase |
| $v_0$ | volume at which the eluate portions are separated |
| w | volume between the intercepts on the base line, of the tangents to the inflection points of the elution curve ($w=4\sigma$) |
| X | inverse function of A |
| x | convenient factor (equation (38) ) |
| $\alpha$ | separation factor (relative volatility) |
| $\beta$ | convenient factor (equation (iii) ) |
| $\Gamma$ | column length required for a peak resolution of unity |
| $\eta$ | various impurity fractions |
| $\sigma$ | standard deviation of elution curve (volume units) |

## APPENDIX

The solution of equation (39) for large values of R: as $R \longrightarrow \infty$, x and $\{(1+p)R-x\}/p$ will both become very large. Since[18]

$$1-A(t)\xrightarrow[\infty]{t}\frac{\exp\{-t^2/2\}}{\sqrt{2\pi}t} \quad \text{(i)}$$

equation (39) is reduced to

$$\sqrt{2\pi}\, m\, \bar{\eta}_m=\frac{m^2 p}{(1+p)R-x}\exp\left\{-\frac{\{(1+p)R-x\}^2}{2p^2}\right\}=\frac{\exp\{-x^2/2\}}{x} \quad \text{(ii)}$$

Let

$$x=R+\frac{\beta}{R} \quad \text{(iii)}$$

Equation (ii) now becomes

$$\begin{aligned}\sqrt{2\pi}\, m\, \bar{\eta}_m R\exp\{R^2/2\}&=\frac{m^2}{1-\beta/pR^2}\exp\{\beta/p-\beta^2/2p^2R^2\}\\&=\exp\{-\beta-\beta^2/2R^2\} \quad \text{(iv)}\end{aligned}$$

$\beta$ may be seen to tend to a finite value as R tends to infinity, and equation (iv) thus reduces to

$$\sqrt{2\pi}\, m\, \bar{\eta}_m R\exp\{R^2/2\}=m^2\exp\{\beta/p\}=\exp\{-\beta\} \quad \text{(v)}$$

from which $\beta$ is given by

$$\beta=\frac{2p}{p+1}\ln\left(\frac{1}{m}\right) \quad \text{(vi)}$$

Substitution of this value in equation (v) yields

$$\bar{\eta}_m=\frac{m^{(p-1)/(p+1)}\exp\{-R^2/2\}}{\sqrt{2\pi}\,R}=m^{(p-1)/(p+1)}\eta_{1:1} \quad \text{(vii)}$$

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# NOTES

## RUTIN FROM *Pachystigma pygmaeum*

*by*

**A. L. CLINGMAN**

Rutin, a flavonol glycoside, has been isolated from the leaves of *Pachystigma pygmaeum* (Schl.) Robyns (gousiektebossie). Rutin is 3-quercetin-rutinoside[1]. It was hydrolysed with acetic acid according to the elegant method of Zemplen and Gerecs[2], to give rutinose, which is 6-0-(β-L-rhamnosyl)-D-glucose[1].

Veldsman[3] isolated a flavonol glycoside from *P. pygmaeum* which was not positively identified.

### EXPERIMENTAL

Paper chromatograms of carbohydrates were developed in ethyl acetate—acetic acid—formic acid—water (18 : 3 : 1 : 4) and were sprayed with *p*-anisidine hydrochloride solution. All melting points are corrected.

*Extraction of flavonol glycoside.* Fresh leaves of *Pachystigma pygmaeum* were extracted with ethanol. A flavonol glycoside was isolated from the leaf extract, purification being effected through the insoluble lead salt[4]. The glycoside was recrystallised from aqueous ethanol, m.p. and mixed m.p. with authentic rutin 188-191·5° (lit.[1, 5] not completely melted at 190°), $[\alpha]_D^{19}+6{\cdot}2$(c, 0·9 in ethanol) (Found: C,49·7; H, 5·7. Calc. for $C_{27}H_{30}O_{16}{\cdot}2H_2O$: C, 50·0; H, 5·3%.) Paper chromatograms of the compound developed in the usual solvents for flavonols gave $R_F$ values identical with those reported[4] for rutin. The infrared spectrum of the compound (potassium bromide disk) and of authentic rutin were identical.

*Hydrolysis of rutin.* The flavonol glycoside (0·506 g) in N-sulphuric acid (25 ml) was heated at 95° for 4 hr. A yellow crystalline precipitate (0·236 g; 100%) was obtained, which, after one recrystallisation from ethanol, had m.p. 289-291·5°. Authentic quercetin (anhydrous) has m.p. 304-306°. The yellow aglycone was acetylated (pyridine-acetic anhydride) to give after recrystallisation from methanol penta-O-acetylquercetin, m.p. and mixed m.p. with authentic material 196·5-197·5° (Found: C, 58·4; H, 3·9; Ac, 38·9. Calc. for $C_{25}H_{20}O_{12}$: C, 58·6; H, 3·9; Ac, 42·0%).

The combined filtrate and washings obtained after removal of the aglycone were neutralised with barium carbonate and concentrated to a residue (0·204 g; 72%). Paper chromatograms of this material gave spots of $R_G$ (relative to galactose) 1·1 (glucose) and 2·9 (rhamnose).

Rutin (6 g) in 10% acetic acid (150 ml) was refluxed gently for 6 hours and then diluted with water (150 ml). The solution was left overnight at 5° and filtered. After addition of charcoal and filtration, it was concentrated (60°/20 mm) to a small volume, diluted with water and again treated with charcoal, and concentrated to dryness (60°/20 mm). A solid was obtained which reduced Fehling's solution and had m.p. 189·5-194°, $[\alpha]_D^{20}$ -10° (c, 0·5 in ethanol). Rutinose is reported[5] as being a non-crystalline powder, m.p. 189-192°, $[\alpha]_D$ -10·0° (ethanol). Paper chromatograms of rutinose and its acid hydrolysate gave spots of $R_G$ 0·3 (rutinose), 1·2 (glucose), and 3·0 (rhamnose). Rutinose was acetylated (sodium acetate-acetic anhydride) to give a product which crystallised from methanol, m.p. 168-170°, $[\alpha]_D^{22}$ -26·3° (c, 0·5 in $CHCl_3$). [Lit.[2] m.p. 169-170°, $[\alpha]_D$ -27·7° ($CHCl_3$)].

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# DISTRIBUTION COEFFICIENTS OF THE ANIONIC THIOCYANATE COMPLEXES OF METAL CATIONS

*by*

**L. D. C. BOK and V. C. O. SCHÜLER**

Several recent papers have appeared dealing with the ion exchange adsorption of metals as anionic complexes. The complexing agents which have been studied include hydrochloric acid[1], nitric acid[2,3], hydrofluoric acid[4,5,6], sulphuric acid[2] and phosphoric acid[7]. In addition, several organic complexing agents such as ethylenediaminetetraacetic acid[8], citrate and oxalate have been employed.

Several applications have been reported of the use of the thiocyanate ion as a complexing agent for the separation of metals on anion exchange columns[9,10]. Markle and Boltz[11] used the adsorption of metal thiocyanate complexes on anion exchange resin as a tool for the elucidation of the nature of the complexes formed when thiocyanate is used as a chromogenic agent in spectrophotometry.

The anionic adsorption characteristics of the thiocyanate complexes of some of the transition group metals are being studied by us. The distribution coefficients of these complexes for the range 0·1M to 2·0M thiocyanate (added as ammonium thiocyanate) in 0·1M hydrochloric acid medium have been determined. In addition to adsorption from aqueous solution, adsorption from 1:1 (v/v) mixtures of water-acetone and water-ethanol solution has been investigated. The results obtained for the various solvents are shown in Figs. 1 to 3. The chemical behaviour of the various metals and their salts mentioned in the figures has been mainly taken from Williams[12] and *The Handbook of Chemistry and Physics*[13].

## EXPERIMENTAL

### *Materials used:*

*Resin*—Rohm and Haas Company Amberlite IRA-400 strongly basic anion exchanger, mean effective size 0·4-0·6 mm.

*Solutions*—The solutions were prepared in such a way that 100 ml contained 1 millimole of the metal salt (as chloride) under test together with the predetermined amount of ammonium thiocyanate as well as the correct amount of hydrochloric acid to give a final concentration of 0·1M hydrochloric acid.

The experimental procedure adopted and the reasons for the choice of solvent have been described previously[10].

The distribution coefficient $K_d$ is defined as:

$$K_d = \frac{\text{millimoles metal on resin}}{\text{millimoles metal in solution}} \times \frac{\text{volume of solution}}{\text{weight of dry resin}}$$

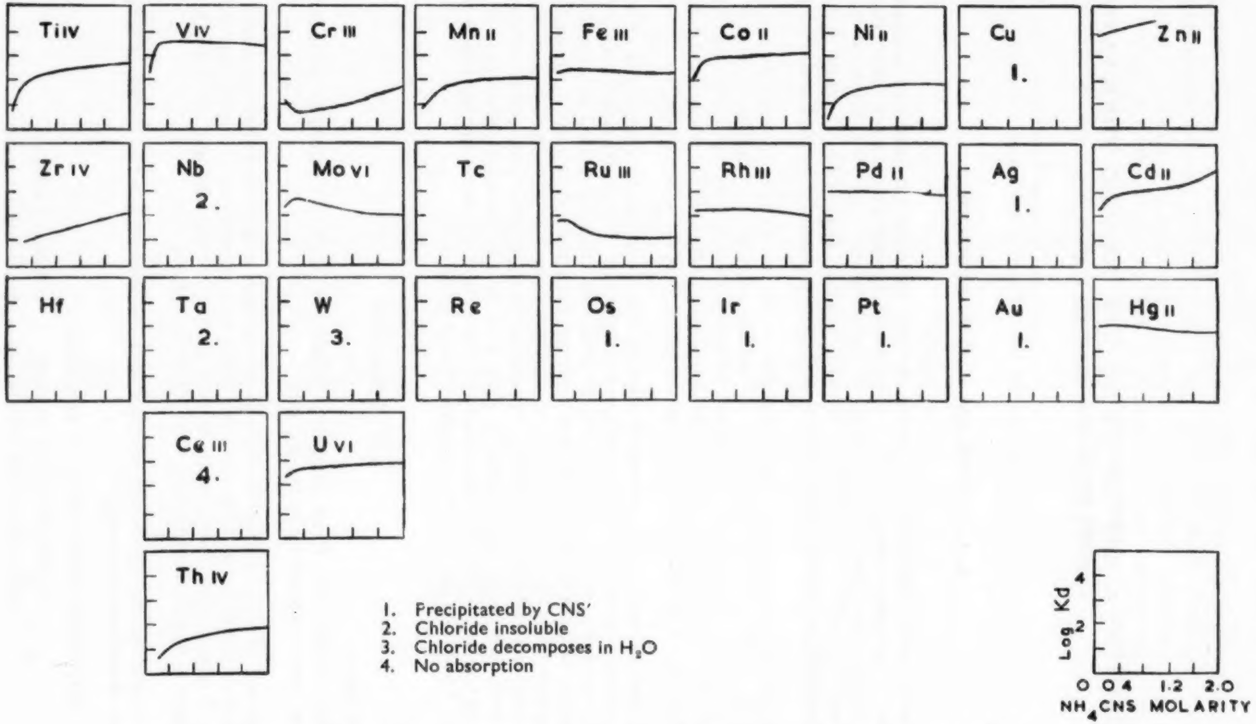


FIG. 1.—Adsorption of metal thiocyanate complexes from aqueous solution (0 1M. hydrochloric acid, Amberlite IRA-400 resin)

*Note.*—Roman numerals refer to oxidation state in initial solution

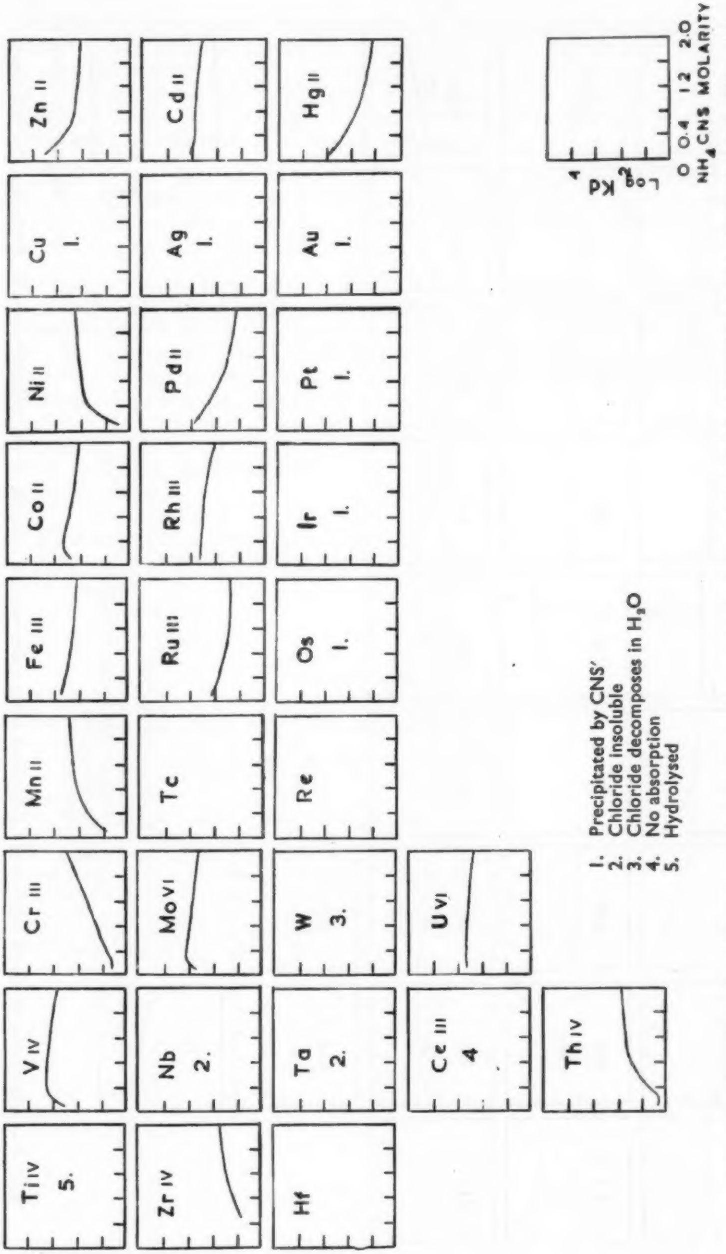
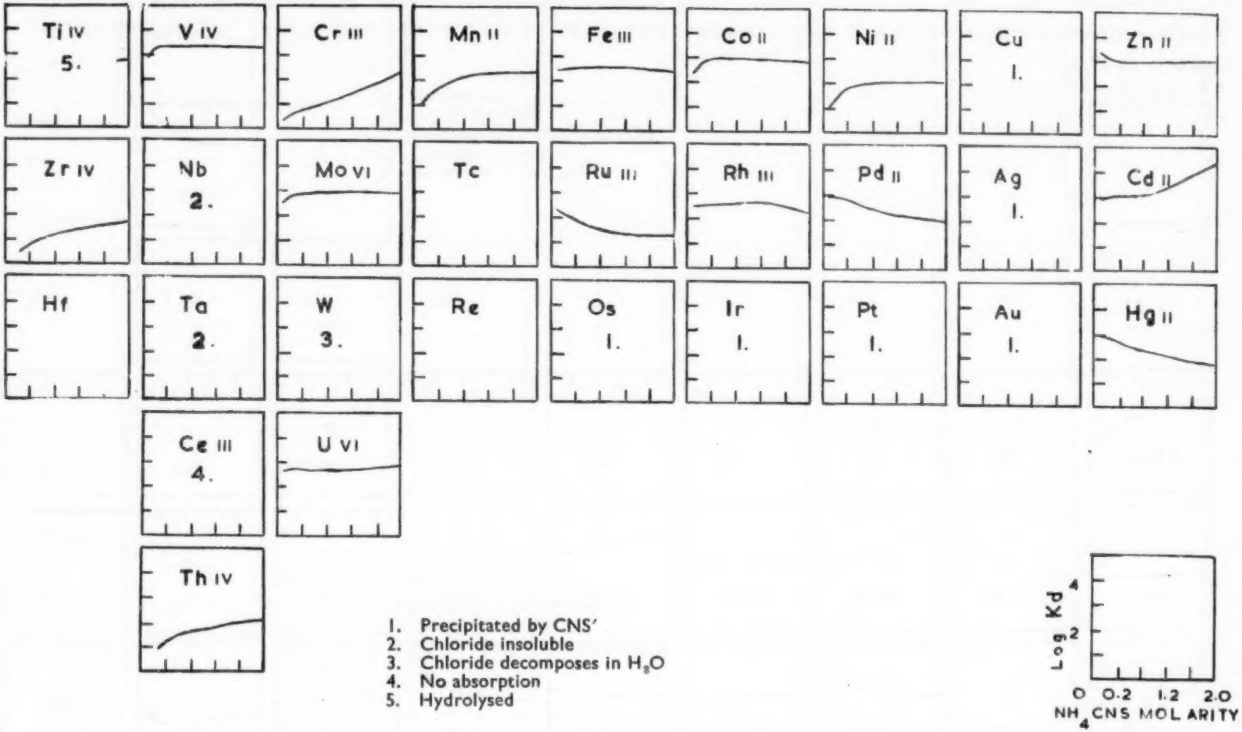


FIG. 2.—Adsorption of metal thiocyanate complexes from water-acetone solution (0·1M hydrochloric acid, Amberlite IRA-400 resin)

*Note.*—Roman numerals refer to oxidation state in initial solution



1. Precipitated by CNS′
2. Chloride insoluble
3. Chloride decomposes in $H_2O$
4. No absorption
5. Hydrolysed

FIG. 3.—Adsorption of metal thiocyanate complexes from water-ethanol solution (0·1M hydrochloric acid, Amberlite IRA-400 resin)

*Note.*—Roman numerals refer to oxidation state in initial solution

To facilitate the graphical representation of the dependence of the distribution coefficient on the concentration of the complexing agent, $\log K_d$ has been plotted against the concentration of the complexing agent used. In general, when $\log K_d$ is equal to or greater than 2, the complex in question will be quantitatively retained on passing a solution of it through a column of the exchanger tested, provided it is first converted to the form of the complexing agent.

A study of the data presented in the three Figs. suggests that many of the transition group metals which form anionic complexes soluble in dilute hydrochloric acid can be quantitatively retained on columns of Amberlite IRA-400 resin, provided columns of suitable dimensions are used.

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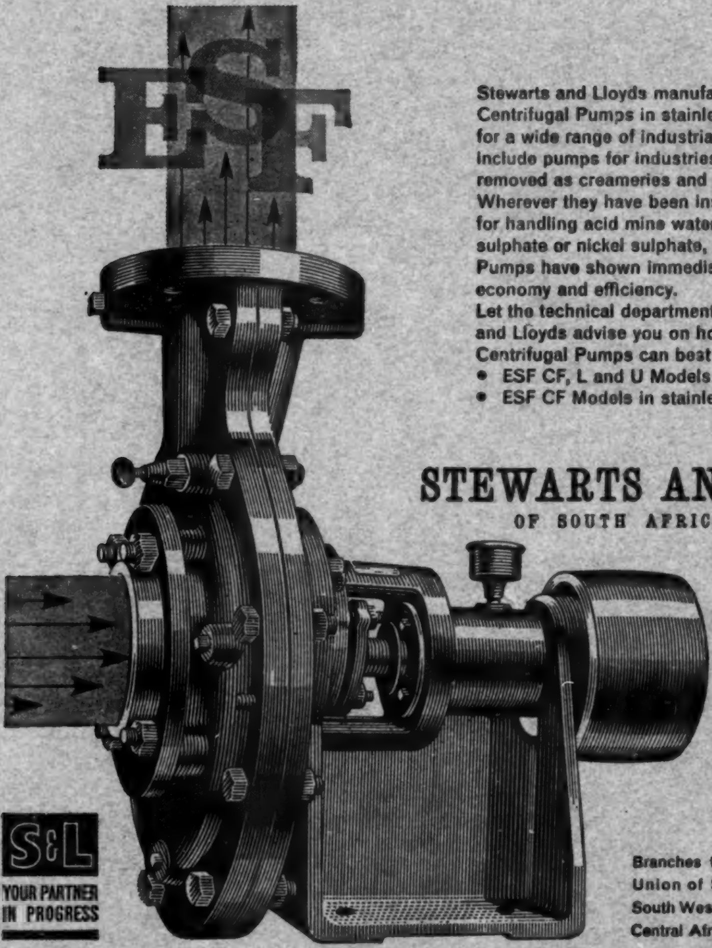

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